Appendix F

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Appendix F

Groundwater Monitoring Data Quality Assessment

F.1 Introduction

This appendix presents the data quality assessment (DQA) for laboratory data generated from groundwater samples collected during calendar year 2013 (CY2013) as part of the Hanford Site groundwater monitoring program. The purpose of this DQA is to determine whether these data meet the data quality requirements specified in *Hanford Site Environmental Monitoring Plan* (DOE/RL-91-50) and *CH2M HILL Plateau Remediation Company Environmental Quality Assurance Program Plan* (CHPRC-00189).

For the groundwater monitoring program during CY2013, 1,186 wells, aquifer tubes, and springs were sampled over the extent of the Hanford Site. These sampling events generated 13,399 samples: 3,263 field samples and 10,136 laboratory samples. From these 13,399 samples, Field Sampling Operations generated 15,544 field measurements, and six analytical laboratories reported 133,108 laboratory results for a total of 148,652 measurements.

F.2 Purpose

The purpose of this DQA is to determine whether the data generated from the CY2013 groundwater monitoring sampling effort meet the data quality requirements specified in the DOE/RL-91-50 and CHPRC-00189. Meeting the data quality requirements of these documents provides assurance that the data collected are of sufficient quantity and quality for the groundwater monitoring program.

F.3 Scope

This DQA focuses on the laboratory chemical and radiochemical data collected for the groundwater monitoring program. The data are evaluated to determine whether they meet the analytical criteria outlined in DOE/RL-91-50 and CHPRC-00189. The DQA methodology includes data verification and data usability evaluations:

- Data verification is the process of evaluating the completeness, correctness, and conformance/
 compliance of a specific data set against the method, procedural, or contractual requirements. It includes
 confirmation that the specified sampling and analytical requirements have been completed as specified
 in DOE/RL-91-50 and CHPRC-00189. This evaluation is documented in Section F.5. In addition,
 verification is performed for field quality control (QC) samples in Section F.8 and for laboratory QC
 samples in Section F.9.
- The data usability assessment is a determination of the adequacy of the data to support the groundwater monitoring program requirements and is based upon the verification results. This evaluation is summarized in Section F.10.

F.4 Groundwater Monitoring Program Analytical Data Quality Requirements

Table F.1 presents the groundwater monitoring program data requirements from DOE/RL-91-50 and CHPRC-00189. QC results for groundwater monitoring samples were evaluated against these requirements as part of this DQA (see Sections F.8 and F.9). The QC samples governed by the QC requirements may be divided into two components: field QC samples and laboratory QC samples. Sections F.4.2 and F.4.3 describe these two types of QC samples.

Table F.1. Quality Control Acceptance Criteria for Groundwater Samples

Table F.1. Quality Control Acceptance Criteria for Groundwater Samples							
Constituent	QC Element	Acceptance Criterion ^a	Corrective Action				
Genera	Chemical Parar	meters	-				
Alkalinity, chemical oxygen demand, conductivity, oil and grease, pH, total dissolved solids, total organic carbon, total organic halides, total petroleum hydrocarbons by GC ^b	MB° LCS DUP MS SUR EB, FTB Field Dup Field Split	<mdl 80% to 120% recovery ≤20% RPD^h 75% to 125% recovery Statistically derived <2 times MDL ≤20% RPD^h ≤20% RPDⁱ</mdl 	Flagged with "C" Data reviewed ^d Data reviewed ^d Flagged with "N" Data reviewed ^d Flagged with "Q" Flagged with "Q" Flagged with "Q"				
Am	monia and Anio	ns					
Ammonia, anions, cyanide	MB LCS DUP MS EB, FTB Field Dup Field Split	$<$ MDL 80% to 120% recovery \le 20% RPD ^h 75% to 125% recovery $<$ 2 times MDL \le 20% RPD ^h \le 20% RPD ⁱ	Flagged with "C" Data reviewed ^d Data reviewed ^d Flagged with "N" Flagged with "Q" Flagged with "Q" Flagged with "Q"				
	Metals						
ICP metals, ICP/MS metals, mercury, uranium	MB LCS MS MSD EB, FTB Field Dup Field Split	$<$ MDL $^{\rm f}$ 80% to 120% recovery 75% to 125% recovery \le 20% RPD <2 times MDL \le 20% RPD $^{\rm h}$ \le 20% RPD $^{\rm i}$	Flagged with "C" Data reviewed ^d Flagged with "N" Data reviewed ^d Flagged with "Q" Flagged with "Q" Flagged with "Q"				
Volatile	e Organic Compo	ounds					
Volatiles by GC-MS	MB LCS MS MSD SUR EB, FTB, FXR Field Dup Field Split	<mdl<sup>g Statistically derived Statistically derived Statistically derived Statistically derived <2 times MDL^g ≤20% RPD^h ≤20% RPDⁱ</mdl<sup>	Flagged with "B" Data reviewed ^d Flagged with "T" Data reviewed ^d Data reviewed ^d Flagged with "Q" Flagged with "Q" Flagged with "Q"				
Semivolatile Organic Compounds							
Herbicides by GC, PCBs by GC, pesticides by GC, phenols by GC, semivolatiles by GC-MS	MB LCS MS MSD SUR EB, FTB Field Dup Field Split	<2 times MDL Statistically derived Statistically derived Statistically derived Statistically derived <2 times MDL ≤20% RPD ^h ≤20% RPD ⁱ	Flagged with "B" Data reviewed ^d Flagged "N" or "T" Data reviewed ^d Data reviewed ^d Flagged with "Q" Flagged with "Q" Flagged with "Q"				

Table F.1. Quality Control Acceptance Criteria for Groundwater Samples

Constituent	QC Element	Acceptance Criterion ^a	Corrective Action					
Radiological Parameters								
Gamma scan, gross alpha, gross beta, iodine-129, plutonium (isotopic), strontium-89/90, technetium-99, tritium, tritium (low level), uranium (isotopic)	MB LCS DUP MS EB, FTB Field Dup Field Split	<2 times MDA 70% to 130% recovery \le 20% RPD ^h 60% to 140% recovery <2 times MDA \le 20% RPD ^h \le 20% RPD ⁱ	Flagged with "B" Data reviewed ^d Data reviewed ^d Flagged with "N" Flagged with "Q" Flagged with "Q" Flagged with "Q"					

Sources: DOE/RL-91-50, Hanford Site Environmental Monitoring Plan, and CHPRC-00189, CH2M HILL Plateau Remediation Company Environmental Quality Assurance Program Plan.

- a. For the laboratory QC types LCS, DUP, MS, MSD, and SUR, laboratory-determined, statistical process-control limits were used when available, otherwise the limits shown is this table were used. For the laboratory duplicate types DUP, LCS duplicate, MSD, and SUR duplicate, the RPD limit of 20% was used if laboratory-determined limits were not available.
- b. The source documents classify total petroleum hydrocarbons as a VOC. Total petroleum hydrocarbons have historically been classified as a general chemical parameter.
- c. Does not apply to pH determinations.
- d. After review, corrective actions are determined on a case-by-case basis. Corrective actions may include a laboratory recheck, rerun, or flagging the associated groundwater monitoring data as suspect (Y flag) or rejected (R flag).
- e. The source documents indicate that field splits with RPDs exceeding 20% are to be Q flagged. Prior to CY2013, field splits were not Q flagged.
- f. The source documents indicate that the method blank is to be compared to the required detection limit (RDL). Because the RDL is not readily accessible in the HEIS database, the MDL was used instead. In most cases, the MDL is less than the RDL. g. For the common laboratory contaminants 2-butanone, acetone, methylene chloride, toluene, and phthalate esters, the acceptance criterion is <5 times the MDL.
- h. The RPD for duplicates is calculated only if at least one of the results is greater than or equal to five times the laboratory MDL or MDA.
- i. The RPD for field splits is calculated only if at least one of the results is greater than or equal to five times the larger MDL or MDA of the two analyzing laboratories.

Data Flags:

- B, C = Possible laboratory contamination (analyte was detected in the associated method blank).
- N = Result may be biased (associated matrix spike result was outside the acceptance limits).
- Q = Problem with associated field quality control sample (field blank, field duplicate, and/or field split results were out of limits).
- T = Result may be biased (associated matrix spike result was outside the acceptance limits; used with GC-MS methods only).

Abbreviations:

DUP	=	laboratory sample duplicate	MB	=	method blank
EB	=	equipment blank	MDA	=	minimum detectable activity
FTB	=	full trip blank	MDL	=	method detection limit
FXR	=	field transfer blank	MS	=	matrix spike
GC	=	gas chromatography	MSD	=	matrix spike duplicate
GC-MS	=	gas chromatography - mass spectrometry	PCB	=	polychlorinated biphenyl
ICP	=	inductively coupled plasma	RDL	=	required detection limit
ICP-MS	=	inductively coupled plasma - mass spectrometry	RPD	=	relative percent difference
LCS	=	laboratory control sample	SUR	=	surrogate

F.4.1 Analyte Reporting Conventions

To conform to the analyte reporting conventions used in the annual report and to provide comparability of analytical results among the reporting laboratories, the following analyte reporting conventions are used in this data quality assessment:

- **Ammonium:** Ammonia, nitrogen-in-ammonia, and nitrogen-in-ammonium results are converted to and evaluated as ammonium ion.
- Nitrate: Nitrogen-in-nitrate results are converted to and evaluated as nitrate.
- Nitrite: Nitrogen-in-nitrite results are converted to and evaluated as nitrite.
- **Phosphate:** Phosphorus-in-phosphate results are converted to and evaluated as phosphate.
- **Strontium-90:** Total-beta-radiostrontium results are evaluated as strontium-90.
- Total organic halides: Total-halogens-(all) results are evaluated as total organic halides.

F.4.2 Field QC Sample Types

Field QC samples are used to assess the precision, repeatability, and potential contamination related to sampling and laboratory activities. Field QC samples include three types of field blanks (equipment blanks, full trip blanks, and field transfer blanks), field duplicates, and split samples. Table F.2 summarizes the various field QC sample types, their required collection frequencies, and the actual collection frequencies. Just as for groundwater samples, preservative reagents specific for the analyte(s) to be determined are added to the field QC sample bottles prior to the collection of the QC samples. All field QC samples are delivered to the laboratory without any differentiation between the field QC samples and actual groundwater samples. Table F.2 describes each type of field QC sample and its collection frequency.

Table F.2. Quality Control Field Samples

		Number of QC Sample	Frequency		
Field QC Sample Type	Number of Well Trips ^a	Sets Collected ^b	Required ^c	Actual ^d	
Full trip blanks	2,487	133	5%	5%	
Field transfer blanks	160 ^e	176	100%	110%	
Equipment blanks	281 ^f	49	10% ^g	17%	
Field duplicates	2,487	170 ^h	5%	7%	
TOC quadruplicates	185 ⁱ	196 ^j	n/r	106%	
TOX quadruplicates	175 ⁱ	176 ^j	n/r	101%	
Field split samples	2,487	75 ^k	as needed	3%	

Table F.2. Quality Control Field Samples

		Number of QC Sample	Frequency		
Field QC Sample Type	Number of Well Trips ^a	Sets Collected ^b	Required ^c	Actual ^d	

- a. Includes trips to wells, aquifer tubes, and springs. Well trips are counted only if they are associated with routine groundwater monitoring results in the HEIS *RESULT* table.
- b. Values listed include only field blanks, field duplicates, and field split sample sets collected for routine groundwater monitoring sampling events. A QC sample set consists of all the QC samples of a particular QC sample type (e.g. full trip blanks or field duplicates) for a given well trip and may contain multiple sample numbers.
- c. Required frequency is from DOE/RL-91-50 and CHPRC-00189.
- d. Actual frequency = 100 x Number of QC Sample Sets / Number of Well Trips.
- e. For each day that volatile organic compound samples are collected, one field transfer blank is required for each lab receiving that day's volatile organic compound samples. Multiple field transfer blanks may be required each day that volatile organic compound samples are collected if these samples are to be shipped to more than one lab for analysis.
- f. Number of sampling events for which non-dedicated sampling equipment was used.
- g. The 10% frequency is for routinely used, non-dedicated sampling equipment. For new types of non-dedicated sampling equipment, the equipment blank frequency is 100% until the decontamination procedure for the new equipment is shown to produce acceptable equipment blank results.
- h. Number of pairs of field duplicate sample sets collected.
- i. Number of well trips for which TOC or TOX samples were collected.
- j. Number of sets of quadruplicate samples collected.
- k. Number of pairs of field split sample sets collected.

n/r = not required
QC = quality control
TOC = total organic carbon
TOX = total organic halides

- Equipment blanks (EB) are samples of reagent water that are pumped or washed through nondedicated sampling equipment. EBs are used to monitor the effectiveness of equipment decontamination procedures and to monitor for contamination associated with field sampling equipment.
- Full trip blanks (FTB) are samples that contain reagent water and any required preservatives. An
 FTB is used to check for contamination in sample bottles and laboratory sample preparation. The
 FTB is analyzed for all constituents of interest and is collected in the same types of sample bottles
 used to collect groundwater samples. The FTB is filled during bottle preparation using the same
 sample preparation used for regular well samples. FTBs are not opened in the field.
- Field transfer blanks (FXR) are analyzed for volatile organic compounds (VOCs) and are used to check for VOC contamination associated with sampling activities. At the time of sample collection, the FXR is filled at the sampling site by pouring reagent water from a cleaned glass container into VOC sample vials pre-loaded with any required preservative. After collection, the FXR is treated in the same manner as the other samples collected during the sampling event. One FXR is collected each day groundwater samples are collected for VOCs. If the VOC samples collected on a given day will be shipped to multiple laboratories, then an FXR is collected for each laboratory for that day.
- Field duplicate samples are replicate samples collected to determine the precision of sampling
 and the laboratory analytical measurement process by comparing results with an identical sample
 collected at the same time and location. Matching field duplicates are stored in separate
 containers and are analyzed as separate samples by the same laboratory.

• Split samples are replicate samples sequentially collected from the same location in the same sampling event and analyzed by different laboratories. Split samples are used to evaluate interlaboratory precision and comparability.

FB results are evaluated by comparison with two times the method detection limit (MDL) or minimum detectable activity (MDA) of the performing laboratory; field blank results that exceed that limit and the results for any samples associated with the FB are given a review qualifier of Q (see Table F.4). Associated samples are those collected on the same day and analyzed by the same method as the corresponding FB.

Field duplicate sample results are evaluated only if at least one result is five times the laboratory MDL or MDA. Split sample results are evaluated only if at least one result is five times the larger of the laboratory MDL or MDA of the two analyzing laboratories. Field duplicate and field split samples that qualify are evaluated using the relative percent difference (RPD) between the duplicate or split sample pair. The RPD is a measure of precision and is calculated as shown in Equation F-1:

RPD =
$$\left| \frac{C_1 - C_2}{(C_1 + C_2)/2} \right| \times 100$$
 (Equation F-1)

where:

 C_I = parent sample analyte concentration or activity

 C_2 = duplicate sample analyte concentration or activity

A perfect match between the parent sample and its duplicate yields an RPD of 0%. Results for field duplicate samples that exceed the RPD limit of 20% are given a review qualifier of Q (see Table F.4). Only the two samples of the duplicate pair are considered to be associated samples. Historically, split samples that exceed the RPD limit have not been Q flagged. However, split samples collected during CY2013 that have results exceeding the RPD limit have been Q flagged. Only the two samples of the split pair are considered to be associated samples.

Total organic carbon (TOC) and total organic halides (TOX) are *Resource Conservation and Recovery Act of 1976* (RCRA) indicator analytes; samples for these analytes are usually taken in quadruplicate (40 CFR 265.92, "Interim Status Standards for Owners and Operators of Hazardous Waste Treatment, Storage, and Disposal Facilities," "Sampling and Analysis"). Field quadruplicate sample results are evaluated only if at least one result is at least five times the laboratory MDL. Field quadruplicate results that qualify are evaluated using the percent relative standard deviation (%RSD) within the quadruplicate sample set. The %RSD is a measure of precision and is calculated as shown in Equation F-2:

$$\% RSD = \frac{\sqrt{\sum_{i=1}^{n} (C_i - \overline{C})^2}}{\overline{C}} \times 100$$
 (Equation F-2)

where:

 $C_i = i^{th}$ sample concentration

 \overline{C} = average sample concentration

n = number of results (usually four)

A perfect match of results within a quadruplicate sample set yields a %RSD of 0%. For any results in a qualifying quadruplicate data set that were less than the laboratory MDL, MDLs were used to compute the %RSD. Quadruplicate split sample results are evaluated only if at least one quadruplicate average is greater than or equal to five times the larger of the laboratory MDLs of the two analyzing laboratories. To determine the precision of a set of split quadruplicate samples, the RPD of the two averages for the quadruplicate split samples is determined and compared to 20%. Results for field quadruplicate samples that exceed a %RSD of 20% or quadruplicate split samples that exceed an RPD of 20% are not given a review qualifier.

F.4.3 Laboratory Quality Control Sample Types

Laboratory quality assurance (QA)/QC requirements govern nearly all aspects of analytical laboratory operation, including instrument procurement, maintenance, calibration, and operation. During the analysis of groundwater samples, laboratory QC samples are used to assess potential sample contamination, precision, and accuracy related to laboratory activities. Laboratory QC samples may include method blanks, laboratory control samples (LCS), laboratory control sample duplicates (LCSD), matrix spike (MS) samples, matrix spike duplicates (MSDs), and surrogates. The following bullets describe each type of laboratory QC sample and the way they are evaluated.

- Laboratory method blanks provide a measure of the cleanliness during sample preparation and analysis. The appearance of measurable analytes in the method blank may indicate contamination of customer samples during the analytical process.
- Laboratory sample duplicates, LCSDs, MSDs, and surrogate duplicates provide a measure of the reproducibility of the analytical process. The RPD is the metric used to determine reproducibility (see Equation F-1). Laboratory sample duplicates qualify for evaluation only if at least one result is five times the laboratory MDL.
- LCSs, MSs, and surrogates contain known amounts of analytes and provide a measure of the accuracy of the analytical process. Percent recovery is the metric used to determine analytical accuracy (see Equation F-3). Percent recoveries consistently less than or greater than 100% may indicate a bias in the analytical process.

These laboratory QC samples are included in sample preparation and analytical batches along with customer samples. An analytical batch typically consists of a maximum of 20 customer samples. The numbers and types of QC samples included in sample batches are dictated by the analytical method being used. Analytical methods usually employ only a subset of the available types of QC samples. At a minimum, most sample preparation and analytical methods include a method blank, one of the duplicate types (e.g., sample duplicate), and one of the standard types (e.g., laboratory control sample).

Laboratory analytical accuracy for LCSs, MSs, and surrogates is evaluated using percent recovery as shown in Equation F-3:

Percent Recovery =
$$\frac{C_m}{C_a} \times 100$$
 (Equation F-3)

where:

 C_m = measured analyte concentration or activity

 C_a = actual, known analyte concentration or activity

Perfect recovery of the measured analyte concentration or activity yields a percent recovery of 100%.

F.4.4 Qualification Flags

During the generation and evaluation of environmental analytical data, any of several qualification flags may be assigned to an individual result. The Hanford Environmental Information System (HEIS) database carries qualification flags applied from three sources: the laboratory (laboratory qualifier), a data reviewer (review qualifier), or a third party data validator (validation qualifier). Table F.3 presents the laboratory qualifier flags and Table F.4 outlines the review qualifier flags. For the CY2013 groundwater monitoring data set, no third party validation was performed, and no validation qualifiers were applied to the data set.

Table F.3. Laboratory Qualifier Data Quality Flags

- 1	Potentian						
Flag	Definition						
В	Inorganics and wetchem* – The analyte was detected at a value greater than or equal to the method detection limit (MDL) but less than the contract required detection limit (CRDL).						
	Organics – The analyte was detected in both the associated method blank and in the sample.						
	Radionuclides – The associated method blank has a result \geq 2x the minimum detectable activity (MDA) and, after corrections, the result is \geq MDA for this sample.						
С	Inorganics and wetchem – The analyte was detected in both the sample and the associated method blank, and the sample concentration was less than or equal to five times the blank concentration.						
D	All – Analyte was determined using a secondary dilution factor greater than one. The primary preparation required additional dilution either to bring the analyte within the calibration range or to minimize interference.						
Е	Inorganics – Reported value is estimated because of interference. See any comments that may be in the laboratory report case narrative.						
	Organics – Concentration exceeds the calibration range of the gas chromatograph - mass spectrometer (GC-MS).						
J	Organics – The analyte was detected at a value greater than or equal to the MDL but less than the CRDL.						
N	All (except GC-MS methods) – The matrix spike recovery is outside control limits. The associated sample data may be biased.						
О	All – The laboratory control sample recovery is outside control limits.						
T	Organics (GC-MS methods only) – The matrix spike recovery is outside control limits. The associated sample data may be biased.						
U	All – The constituent was analyzed for but was not detected.						
X	All – Indicates a result-specific comment is provided in the data report and/or case narrative.						

^{*} Wetchem is a miscellaneous group of analytical methods such as the colorimetric determination of hexavalent chromium, the titrimetric determination of alkalinity, or the distillation and titrimetric determination of sulfide.

Table F.4. Review Qualifier Data Quality Flags

Flag	Definition
A	Indicates an issue with the chain of custody that could affect data integrity.
F*	Result is undergoing further review. This review qualifier is assigned when a Request for Data Review (RDR) is first processed.
G*	Result has been reviewed through the RDR process and determined to be correct, or the laboratory has supplied a corrected result after reviewing the original result or after reanalyzing the sample.
Н	Laboratory holding time was exceeded before the sample was analyzed.
P*	Potential problem. Collection/analysis circumstances make the result questionable.
Q	An associated QC sample is out of limits; the associated sample number is listed in the Result Comment field for the Q-flagged result. See Section F.4.2 for the definition of associated samples.
R*	Do not use. Further review indicates the result is not valid. This review qualifier is used only when documented evidence exists that the result is not valid. Generally, results that are "R" qualified will be excluded from statistical evaluations, maps, and other interpretations.
Y*	Result is suspect. Review had insufficient evidence to show result valid or invalid.
Z*	Miscellaneous circumstance exists. Additional information for this record may be found in the Result Comment field in the HEIS Result table and/or in the Sample Comment field in the HEIS Sample table.

^{*} These flags are applied as part of the Request for Data Review process.

Of the review qualifier flags, the Request for Data Review (RDR) process most commonly generates F, G, R, and Y flags (see Table F.4). The F flag indicates the analytical result is under review within the RDR process; an F flag is typically resolved to a G flag, R flag, or Y flag during the RDR process. The G flag indicates that the result has been reviewed within the RDR process and determined to be valid. In some cases, the G flag is applied to a result after the old, reviewed result has been replaced by a new value from the laboratory; the new laboratory value may be a correction of the originally reported value or may be from a re-analysis of the sample. The R flag indicates the analytical result has been reviewed and rejected as invalid based upon a known reason such as an instrument calibration failure. The Y flag indicates the analytical result has been reviewed and is considered questionable based on additional evidence, such as a result that does not fit with the historical trend for the sample source and is inconsistent with related parameters.

The Q flag review qualifier is applied to the analytical results of those samples associated with field QC samples having analytical results that exceed the QC criteria given in DOE/RL-91-50 and CHPRC-00189 and outlined in Table F.1. Associated samples are defined in Section F.4.2.

F.5 Data Completeness

Data completeness is a measure of how much of the data set is judged to meet the quality criteria and thus is useable for the groundwater monitoring program. The completeness goal is determined as a percentage of data judged "good" versus all data collected for the program and is set at a minimum of 85% ¹ (DOE/RL-91-50). Completeness statistics are calculated and presented for:

- the percentage of successful sampling events during CY2013 versus the number of scheduled sampling events,
- the percentage of field QC samples collected versus the number of QC samples required, and
- the percentage of the data set that meets quality criteria.

F.5.1 Percentage of Successful Sampling Events

During CY2013, 2,735 sampling events were planned, and 2,712 sampling events were successfully executed for a sampling event completion rate of 99.2%. These sampling events include 235 CY2013-scheduled events sampled either in CY2012 or in CY2014. Sources sampled included wells, aquifer tubes, and springs. This completion rate indicates that sufficient sampling events were completed to meet groundwater monitoring program requirements. The 2,487 well trips listed in Table F.2 reflect only those CY2013 sampling events that resulted in groundwater monitoring field and laboratory data appearing in the HEIS *RESULT* table.

F.5.2 Percentage of Field Quality Control Samples Collected

The types and collection frequencies of field QC samples for the groundwater monitoring program are given in DOE/RL-91-50 and CHPRC-00189; the collection of quadruplicate samples at RCRA sites for TOC and TOX is mandated by 40 CFR 265.92. Section F.4.2 gives a more complete discussion of field QC samples. Table F.2 summarizes those QC types, their required collection frequencies, and the actual collection frequencies. The table indicates that the requirements for the minimum collection frequencies for groundwater monitoring field QC samples were met during CY2013.

To determine the collection frequency for EBs, the only non-dedicated sampling equipment currently tracked in the electronic database are "Bailer", "Kabis", and "Portable Grundfos". Non-dedicated sampling manifolds are also used for collection of some groundwater samples, but are not tracked in the database. Consequently, the number of well trips for EBs reported in Table F.2 underestimates the actual number of well trips that use non-dedicated sampling equipment, and the actual sampling frequency for EBs is less than 17%. Until the use of non-dedicated sampling manifolds is tracked, a more accurate estimate of the actual sampling frequency for EBs is unavailable.

For the TOC and TOX quadruplicate samples, the sampling frequency is slightly greater than 100% due to the collection of eleven split sample sets for TOC and a single split sample set for TOX.

F.5.3 Percentage of Useable Data

This section provides an overview of data usability; subsequent sections provide detailed information regarding data compliance with quality requirements.

Table F.5 summarizes the percentage of useable groundwater monitoring data generated from samples collected during CY2013; overall data completeness is 97.4%. This is well above the data completeness goal of 85% as specified in DOE/RL-91-50 and indicates that the large majority of data collected for the

¹ DOE/RL-91-50 defines this completeness goal on a quarterly basis. For this data quality assessment, the completeness goal is applied over the entire calendar year.

groundwater monitoring program is useable. The CY2013 data completeness rate of 97.4% is similar to the 96.6% rate of CY2012 and the 96.8% rate of CY2011.

Data completeness was judged on the following:

- F, R, and Y review qualifier flags associated with the data²,
- Q-flag review qualifiers for data associated with FBs exhibiting possible contamination, data with poor field-sample-duplicate reproducibility, or data with poor field-split reproducibility,
- samples with missed holding times, and
- samples with laboratory qualifiers indicating MB contamination.

Table F.5. Data Completeness Summarized by Method.								
HEIS Method Name	Total Results ^a	Results in Review ^b	Suspect Results ^c	Rejected Results ^d	Field QC Flags	Missed Holding Time	Method Blank Qualifiers	Results Flagged ^e
	O	verall Per	cent Comp	lete = 97.4	%			
Overall Totals:	148,652	33	225	215	2,480	109	1,048	3,885
Ge	neral Chen	nical Paraı	meters: Pe	ercent Com	plete =	98.6%		
Totals	19,858	6	28	19	112	29	83	274
120.1_CONDUCT	13	_	_	_	_	_	_	0
150.1_PH	16	_	ı			16		16
160.1_TDS	1	_	_	_	_	_	_	0
1664A_OILGREASE	2	_			l	_		0
2320_ALKALINITY	1,808	1	2	5	11	1		19
2540C_TDS	81	_		1	8		1	10
310.1_ALKALINITY	22		1		1	_		1
360.1_OXYGEN	2	_			l	_		0
360.1_OXYGEN_FLD	1,522	_	2	1	l			3
410.4_COD	35		1			_		0
4500B_PH	16	_	-			4		4
8015M_TPH_GC	8	_			l			0
9020_TOX	869	4		2	69	_		75
9060_TOC	1,260	_	4	1	21	8	82	114
9223_COLIFORM	32	_	_		2	_		2
CONDUCT_FLD	3,252	1	7	2	_	_	_	10
PH_ELECT_FLD	3,256		4	2		_	_	6
REDOX_PROBE_FLD	999	_	_	1	_	_	_	1
TEMP_FLD	3,254	_	8	2	_	_		10
TURBIDITY_FLD	3,240	_	1	2		_	_	3

² The F flag review qualifier ("result in review") was included in the assessment of CY2013 groundwater monitoring results for this report. After the RDR review, F-flagged results will be resolved to one of the other RDR flags as appropriate.

Table F.5. Data Completeness Summarized by Method.

Table	Table F.5. Data Completeness Summarized by Method.							
HEIS Method Name	Total Results ^a	Results in Review ^b	Suspect Results ^c	Rejected Results ^d	Field QC Flags	Missed Holding Time	Method Blank Qualifiers	Results Flagged ^e
WTPH_DIESEL	131	_	_		_	_	_	0
WTPH_GASOLINE	39	_	_	_	_		_	0
	Ammonia	and Anio	ns: Perce	nt Complet	e = 98.2	%		
Totals	11,453	1	22	15	130	37	21	208
300.0_ANIONS_IC	10,864	1	15	14	90	33	_	149
300.7_CATIONS_IC	52	_	_	_	_		_	0
4500D_SULFIDE	23	_	_				_	0
4500E_CN	215	_	1		8		_	9
9012_CYANIDE	32	_	_				3	3
9034_SULFIDE	105	_	5	1	31	_	18	41
9056_ANIONS_IC	162	_	1	_	1	4	_	6
	M	etals: Per	cent Comp	olete = 96.2	2%	<u></u>		
Totals	67,422	19	165	106	1,581	43	878	2,594
200.8_METALS_ICPMS	19,339	14	95	51	699	12	344	1,163
6010_METALS_ICP	44,406	3	67	53	825	_	502	1,306
6010_METALS_ICP_TR	972	_	_	_	24	_	13	37
6020_METALS_ICPMS	946	_	_	_	33		18	49
7196_CR6	1,708	2	3	2	_	31	1	39
7470_HG_CVAA	7	_	_	_	_		_	0
COLOR_TK_CR6_FLD	9	_	_				_	0
COLOR_TK_FE_FLD	10	_	_	_	_		_	0
UTOT_KPA	25	_	_	_	_		_	0
Vo	latile Orga	nic Comp	ounds: Pe	rcent Com	plete = :	97.6%		
Totals	25,003	3	1	58	516	0	32	607
8015_VOA_GC	40	_	_	_	4	_	_	4
8260_VOA_GCMS	24,951	3	1	58	512		32	603
RSK175_VOA_HDSPC_GC	12	_	_	_	_		_	0
Semi-Volatile Organic Compounds: Percent Complete = 99.9%								
Totals	15,848	0	0	0	5	0	16	19
8041_PHENOLIC_GC	476	_	_	_	_	_	_	0
8081_PEST_GC	786	_	_	_	_	_	_	0
8082_PCB_GC	175	_	_	_	_	_	_	0
8270_SVOA_GCMS	14,011	_	_	_	2	_	10	12
8310_SVOA_HPLC	400	_	_	_	3	_	6	7

Table F.5. Data Completeness Summarized by Method.

I able i		Results		Summar	Field	Missed	Method	D 1/2
HEIS Method Name	Total Results ^a	in Review ^b	Suspect Results ^c		QC Flags	Holding Time	Blank Qualifiers	Results Flagged ^e
Radiological Parameters: Percent Complete = 98.0%								
Totals	9,068	4	9	17	136	0	18	183
906.0_H3_LSC	41	_	_	_	6	_	_	6
906.0ML_H3_LSC	27	_	1	_			_	1
9310_ALPHABETA_GPC	76	_	_	_	2		_	2
ALPHA_GPC	736	1	1	_	13	_	_	15
AMCMISO_IE_PREC_AEA	8	_	_	_	2	_	_	2
BETA_GPC	918	2	1	_	41	_	_	44
C14_CHEM_LSC	26				ı	_	_	0
C14_LSC	262	_	_	1	10	_	_	11
GAMMA_GS	3,023	_	5	10		_	_	15
GAMMALL_GS	370	_	_	_		_	_	0
I129_SEP_LEPS_GS	5	_	_	_		_	_	0
I129LL_SEP_LEPS_GS	432	_	1	1	4	_	12	17
NP237_IE_PRECIP_AEA	11	_	_	_		_	_	0
PUISO_IE_PRECIP_AEA	92	_	_	_		_	2	2
PUISO_PLATE_AEA	59	_	_	_	1	_	_	0
SE79_SEP_IE_LSC	19	_	_	_	9	_	_	9
SRISO_SEP_PRECIP_GPC	26	_	_	_	1	_	_	1
SRTOT_SEP_PRECIP_GPC	772	_	_	1	19	_	4	24
TC99_3MDSK_LSC	787	1	_	2	15	_	_	18
TC99_EIE_LSC	11	_	_	_		_	_	0
TC99_ETVDSK_LSC	36			_	1	_	_	1
TC99_SEP_LSC	20			_	_	_	_	0
THISO_IE_PLATE_AEA	24	_	_	_	5	_	_	5
TRITIUM_DIST_LSC	7	_	_	_	_	_	_	0
TRITIUM_EIE_LSC	1,193	_	_	2	6	_	_	8
UISO_IE_PRECIP_AEA	78	_	_	_	2	_	_	2
UISO_PLATE_AEA	9		_		_	_	_	0

a. Groundwater monitoring results were pulled from the HEIS on April 2, 2014, and include both field and laboratory results.

Of the 148,652 total results noted in Table F.5, 97.4% met QC requirements. Of the 3,885 QC failures summarized in the table, 63.8% of the results were due to out-of-limit field QC and were Q-flagged, and 27.0% were due to out-of-limit method blanks. Of the 2,480 Q-flagged results, 83.2% were Q-flagged for associated out-of-limit field blanks, 10.1% for field duplicates exceeding the RPD limit, and 7.3% for

b. Results in review have a review qualifier of F.

c. Suspect results have a review qualifier of Y.

d. Rejected results have a review qualifier of R.

e. The value in the *Results Flagged* column may be less than the sum of the values in the individual flag columns if the same result has multiple QC issues.

field splits exceeding the RPD limit. These Q-flag percentages may sum to greater than 100% because a result may be flagged for multiple field QC issues (e.g. out-of-limit field blank and out-of-limit field duplicate). Details of the issues associated with these QC failures are provided in subsequent sections.

The poorest completion rate was 96.2% for metals; most of the failures were for metals determined by inductively coupled plasma - atomic emission analysis (EPA Method 6010) and inductively coupled plasma - mass spectrometry (EPA Methods 200.8 and 6020). Of the QC failures for metals, 60.9% were due to Q-flag review qualifiers for data associated with contaminated FBs and poor field duplicate/field split reproducibility. The metals with 100 or more Q-flagged results were sodium (281 of 2,854 results), potassium (195/2,854), copper (119/3,323), chromium (108/3,276), manganese (105/3,025), iron (103/2,860) and calcium (102/2,854). Most (83.2%) of the Q flags were applied for contamination of an associated FB. Method blank contamination accounted for 33.8% of the metals QC failures. The metal most associated with out-of-limits method blanks was potassium with 278 results qualified for method blank failures.

After metals, VOCs had the next poorest completion rate at 97.6%. The VOC most often flagged with QC failures was methylene chloride: 58.0% (469 of 809 results) of the methylene chloride results received a QC flag with nearly all due to apparent FB contamination. Methylene chloride is strongly suspected to be a contaminant in the source deionized water used to generate VOC FBs and may explain most of the Q-flagged methylene chloride results (SGW-52194, *Volatile Organic Compound Contamination in Groundwater Samples and Field Blanks*). A corrective action is underway to add a charcoal polishing stage to the deionized water system to remove VOC contaminants from the blank water supply. All the reported methylene chloride results for groundwater samples associated with contaminated field blanks were less than the MDL. Other VOCs that exhibited 10 or more QC failures were acetone (30/809), trichloroethene (18/809), carbon tetrachloride (12/809), and benzene (11/809).

The remaining completion rates were 98.6% for the general chemical parameters, 98.2% for ammonia and anions, 99.9% for the semivolatile organic compounds, and 98.0% for the radiochemical parameters.

F.6 Laboratory Information and Analytical Methods

Samples collected for the groundwater monitoring program were sent to the six laboratories described in Section F.6.1 for analysis. Each sample is tracked by a unique HEIS database number. Analytical requests for chemical and radiochemical services to be completed by the laboratories were documented on the chain-of-custody forms. Analytical results provided by the laboratories were documented by sample data group (SDG) in data packages. The analytical results were also electronically uploaded and stored in the HEIS database.

F.6.1 Laboratory Information

The samples collected were analyzed at the following six laboratories:

- 222-S Laboratory (222-S, Hanford Site, managed by Advanced Technologies and Laboratories International, Inc.) provided sample analysis for chemical constituents; 222-S generated about 0.1% of the analytical laboratory results.
- Eberline Services (Richmond, California) provided sample analysis for radiochemical constituents; Eberline Services generated less than 0.1% of the analytical laboratory results.
- GEL Laboratories, LLC (GEL, Charleston, South Carolina) provided sample analysis for chemical and radiochemical constituents; GEL Laboratories generated about 0.9% of the analytical laboratory results.

- TestAmerica Richland (TARL, Richland, Washington) provided sample analysis for chemical and radiochemical constituents; TARL generated 1.3% of the analytical laboratory results.
- TestAmerica St. Louis (TASL, St. Louis, Missouri) provided sample analysis for chemical and some radiochemical constituents; TASL generated 4.5% of the analytical laboratory results.
- Waste Sampling and Characterization Facility (WSCF, Hanford Site, managed by Mission Support Alliance, LLC) performed chemical and radiochemical analyses on groundwater samples. WSCF generated 93.1% of the analytical laboratory results.

Sections F.8 and F.9 discuss the analytical data provided by these laboratories.

F.6.2 Analytical Methods

For the analysis of chemical constituents, the analyzing laboratories used standard methods from EPA, ASTM International (formerly American Society for Testing and Materials), and the American Public Health Association. For radiological constituents, the analyzing laboratories employed methods that are recognized as acceptable within the radiochemical industry.

Samples were analyzed using the methods listed in Table F.6. Both single-component and multiple-component analytical methods were used. Single-component analytical methods, such as EPA Method 9030 for sulfide or EPA method 7470 for mercury, yield a single analytical result per analysis. Multi-component analytical methods, such as EPA Method 200.8 for inductively coupled plasma - mass spectrometry metals or EPA method 8260 for gas chromatography - mass spectrometry for VOCs, yield results for multiple analytes per analysis. Multi-component methods may generate results for both target and non-target analytes.

Table F.6. Analytical Methods

Parameter	Analytical Method	Source
Ger	neral Chemical Parameters	_
Alkalinity	EPA Method 310.1	EPA ^a
Alkalinity	Standard Method 2320	Standard Methods ^b
Chemical Oxygen Demand	EPA Method 410.4	EPA ^c
Coliform	Standard Method 9223	Standard Methods ^b
Dissolved Oxygen	EPA Method 360.1	EPA ^a
Oil and Grease	EPA Method 1664A	EPA^d
pН	EPA Method 150.1	EPA ^a
pH	Standard Method 4500B	Standard Methods ^b
Specific Conductivity	EPA Method 120.1	EPA ^a
Total Dissolved Solids	EPA Method 160.1	EPA ^a
Total Dissolved Solids	Standard Method 2540C	Standard Methods ^b
Total Organic Carbon (TOC)	EPA Method 9060	EPA ^e
Total Organic Halides (TOX)	EPA Method 9020	EPA ^e
Total Petroleum Hydrocarbons	EPA Method 8015 (modified)	EPA ^e
Total Petroleum Hydrocarbons - Diesel	NWTPH-D	Washington State Department of Ecology ^f
Total Petroleum Hydrocarbons - Gasoline	NWTPH-G	Washington State Department

Table F.6. Analytical Methods

Parameter	Analytical Method	Source		
	,	of Ecology ^f		
Anions by Ion Chromatography	Ammonia and Anions EPA Method 300.0	EPA ^g		
Anions by Ion Chromatography	EPA Method 9056	EPA ^e		
Cations by Ion Chromatography	EPA Method 300.7	EPA ^h		
Cyanide	EPA Method 9012	EPA ^e		
Cyanide	Standard Method 4500E-CN	Standard Methods ^b		
Sulfide	EPA Methods 9034	EPA ^e		
Sulfide	Standard Method 4500D-Sulfide	Standard Methods ^b		
	Motolo			
Hexavalent Chromium	Metals EPA Method 7196	EPA ^e		
Mercury	EPA method 7470	EPA ^e		
Metals by ICP-AES	EPA Method 6010	EPA ^e		
Metals by ICP-MS	EPA Method 200.8	EPA^{i}		
Metals by ICP-MS	EPA Method 6020	EPA ^e		
Uranium	ASTM D5174	ASTM		
V	olatile Organic Compounds			
Non-Halogenated Volatiles by GC	EPA Method 8015	EPA ^e		
Non-Halogenated Volatiles by Headspace	EPA Method RSKSOP-175	EPA		
Equilibrium - GC Volatile Organic Compounds by GC-MS	EPA Method 8260	EPA ^e		
Sem	ivolatile Organic Compounds			
Organochlorine Pesticides	EPA Method 8081	EPA ^e		
Phenols	EPA Method 8041	EPA ^e		
Polychlorinated Biphenyls	EPA Method 8082	EPA ^e		
Polynuclear Aromatic Hydrocarbons	EPA Method 8310	EPA ^e		
Semivolatile Organic Compounds	EPA Method 8270	EPA ^e		
	Radiological Parameters			
Americium-Curium Isotopes	Ion-exchange Separation/Precipitation/AEA	Lab Specific		
Carbon-14	Chemical Oxidation/LSC	Lab Specific		
Gamma-Emitting Isotopes	Gamma Energy Analysis	Lab Specific		
Gross Alpha-Beta by GPC	Gas Proportional Counter	Lab Specific		
Gross Alpha-Beta by GPC	EPA Method 9310	EPA ^e		
Iodine-129	Separation/Precipitation/LEPS	Lab Specific		
Neptunium-237	Ion-exchange Separation/Precipitation/AEA	Lab Specific		

Table F.6. Analytical Methods

Parameter	Analytical Method	Source
Plutonium Isotopes	Ion-exchange Separation/Precipitation/AEA	Lab Specific
Plutonium Isotopes	Separation/Electroplate/AEA	Lab Specific
Selenium-79	Ion-exchange Separation/LSC	Lab Specific
Strontium-90	Separation/Precipitation/GPC	Lab Specific
Strontium-90 (total-beta radiostrontium)	Separation/Precipitation/GPC	Lab Specific
Technetium-99	Disk Separation/LSC	Lab Specific
Technetium-99	Ion-exchange Separation/LSC	Lab Specific
Thorium Isotopes	Ion-exchange Separation/Electroplate/AEA	Lab Specific
Tritium	EPA Method 906.0	EPA
Tritium	Ion-exchange Purification/LSC	Lab Specific
Tritium	Distillation/LSC	Lab Specific
Uranium Isotopes	Ion-exchange Separation/Precipitation/AEA	Lab Specific
Uranium Isotopes	Separation/Electroplate/AEA	Lab Specific

a. EPA-600/4-79-020, Methods for Chemical Analysis of Water and Wastes.

AEA = alpha energy analysis

ASTM = ASTM International (formerly American Society for Testing and Materials)

EPA = U.S. Environmental Protection Agency

GPC = gas-flow proportional counter
LEPS = low-energy photon spectroscopy
LSC = liquid scintillation counting

b. APHA/AWWA/WEF, 2012, Standard Methods For the Examination of Water and Wastewater.

c. O'Dell, 1993, Method 410.4 The Determination of Chemical Oxygen Demand by Semi-Automated Colorimetry.

d. EPA-821-R-98-002, Method 1664, Revision A: N-Hexane Extractable Material (HEM; Oil and Grease) and Silica Gel Treated N-Hexane Extractable Material (SGT-HEM; Non-polar Material) by Extraction and Gravimetry.

e. SW-846, Test Methods for Evaluating Solid Waste: Physical/Chemical Methods, Third Edition; Final Update IV-B.

f. ECY 97-602, Analytical Methods for Petroleum Hydrocarbons.

g. EPA/600/R-93/100, Methods for the Determination of Inorganic Substances in Environmental Samples.

h. Peden, 1986, Methods for Collection and Analysis of Precipitation.

i. EPA-600/R-94/111, Methods for the Determination of Metals in Environmental Samples, Supplement I.

F.7 Sample Preservation and Holding Times

Sample preservation and holding times are designed to ensure the analytical results generated from a sample are representative of the sample's source. Sample preservation is any method used to ensure the analyte of interest is not altered between the time the sample is acquired and the time it is analyzed. Sample preservation includes selecting the correct sample container material (such as plastic or glass), and may include cooling the sample to \leq 6°C, adjusting the sample pH with acids or bases, or adding other chemicals (such as sodium bisulfite) to prevent oxidation of the analyte of interest. Typically, any preservation chemicals are added to the sample container during container preparation prior to taking the container to the sample site.

Holding times are defined as the time from sample collection or sample extraction to sample analysis. An extraction holding time is the time from sample collection to sample extraction. Holding times are calculated from the date of sample collection as recorded on the sample's chain of custody. Analytes that may change quickly with time, such as coliform or hexavalent chromium, have short holding times while other analytes, such as acid-preserved metals and radionuclides, have much longer holding times.

Table F.7 lists the sample preservation and holding time requirements for the groundwater monitoring program. Upon receipt of a groundwater sample set, the analyzing laboratory inspects the contents of the sample set container, usually an ice chest, to ensure that the samples received reflect what is listed on the accompanying chains of custody. During the receipt inspection, the samples are usually checked for any anomalies, such as missing samples, broken sample bottles, or absent tamper tape. The as-received sample temperature is also usually checked. Samples that are received immediately from the field will not have had time to cool to a preservation temperature $\leq 6^{\circ}$ C; in this circumstance, the as-received condition of the samples is noted and normal processing of the samples for analysis proceeds. Either at the time of receipt, or immediately before sample preparation and analysis, the pH of samples that require pH adjustment is checked to ensure the sample was properly preserved. If the pH is not correct for the sample type (e.g., pH is greater than 2 for ICP metals or is less than 12 for cyanide samples), then the laboratory notes the anomaly and may perform adjustment of the sample pH. Any anomalies noted during sample receiving or with sample preservation are reported to the Soil and Groundwater Remediation Project via Sample Issue Resolution requests. If the Project does not deem the anomaly will affect the sample results, the laboratory is instructed to proceed with the analysis. The Project may decide that the anomaly (e.g., a cyanide sample with a pH less than 12) could jeopardize the integrity of the sample results; in this instance, the laboratory will be instructed to cancel the sample analysis.

Table F.7. Groundwater Sample Container, Preservative, and Holding Time Requirements

Parameter	Container	Preservative	Holding Time	Source		
		General Chemical Parameters	_			
Alkalinity	G/P	Cool to ≤6 °C	14 days	40 CFR 136, Table II		
Chemical oxygen demand	G/P	Cool to ≤6 °C; H ₂ SO ₄ to pH <2	28 days	40 CFR 136, Table II		
Coliform	G/P	Cool to ≤10 °C; 0.0008% Na ₂ S ₂ O ₃	8 hours	40 CFR 136, Table II		
Dissolved oxygen	G	None	as soon as possible	40 CFR 136, Table II		
Hydrogen ion (pH)	G/P	None	as soon as possible	40 CFR 136, Table II		
Oil and grease / Hexane extractable material	G	Cool to ≤6 °C; HCl or H ₂ SO ₄ to pH <2	28 days	SW-846, Table 3-2		
Specific conductance	G/P	None	28 days	40 CFR 136, Table II		
Total dissolved solids	G/P	Cool to ≤6 °C	7 days	APHA/AWWA/WEF, 2012, SM 2540c		
Total organic carbon	aG	Cool to ≤6 °C; HCl or H ₂ SO ₄ to pH <2	28 days	40 CFR 136, Table II		
Total organic halides	G	Cool to ≤6 °C; H ₂ SO ₄ to pH <2	28 days	SW-846, method 9020B		
Total Petroleum Hydrocarbons	aGs	Cool to ≤6 °C; HCl or H ₂ SO ₄ to pH <2	14 days	SW-846, Table 4-1		
Total Petroleum Hydrocarbons - Diesel	aGs	Cool to ≤6 °C; HCl to pH<2	14 days before extraction, 40 days after extraction	ECY 97-602		
Total Petroleum Hydrocarbons - Gasoline	aG	Cool to ≤6 °C; HCl to pH<2	14 days	ECY 97-602		
		Ammonia and Anions				
Cyanide	G/P	Cool to ≤6 °C; 50% NaOH to pH>12	14 days	SW-846, Table 3-2		
Bromide, Chloride, Fluoride, Sulfate	G/P	Cool to ≤6 °C	28 days	SW-846, Table 3-2		
Nitrate, Nitrite, Phosphate	G/P	Cool to ≤6 °C	48 hours	SW-846, Table 3-2		
Sulfide	G/P	Cool to ≤6 °C; zinc acetate and NaOH to pH >9	7 days	SW-846, Table 3-2		
		Metals				
Hexavalent chromium	G/P	Cool to ≤6 °C	24 hours	SW-846, Table 3-2		
Mercury	G/P	HNO₃ to pH<2	28 days	SW-846, Table 3-2		
All other metals	G/P	HNO₃ to pH<2	6 months	SW-846, Table 3-2		
		Volatile Organic Compounds				
Volatile Organic Compounds	aGs	Cool to ≤6 °C; HCl or H ₂ SO ₄ to pH <2	14 days	SW-846, Table 4-1		

Table F.7. Groundwater Sample Container, Preservative, and Holding Time Requirements

Table 1.7.		ipie Container, Freservative, and no	'	
Parameter	Container	Preservative	Holding Time	Source
	s	Semivolatile Organic Compounds		
Semivolatile organic compounds, Organochlorine pesticides and herbicides	aG / PTFE-lined cap	Cool to ≤6 °C	7 days before extraction, 40 days after extraction	SW-846, Table 4-1
Phenols	aG / PTFE-lined cap	Cool to ≤6 °C; 0.008% Na ₂ S ₂ O ₃	7 days before extraction, 40 days after extraction	40 CFR 136, Table II
Polychlorinated biphenyls	aG / PTFE-lined cap	Cool to ≤6 °C	None	SW-846, Table 4-1
Polychlorinated dibenzo-p-dioxins, Polychlorinated dibenzofurans	aG / PTFE-lined cap	Cool to ≤6 °C	30 days before extraction, 45 days after extraction	SW-846, methods 8280 & 8290
		Radiological Parameters		
Gross alpha, Gross beta	G/P	HNO ₃ to pH<2	6 months	SW-846, Table 2-40(B)
Carbon-14, Tritium	G	None	6 months	Laboratory procedure
Americium isotopics, Gamma spectroscopy radionuclides, Plutonium isotopics, Radium isotopics, Strontium-90, Uranium isotopics		HNO₃ to pH<2	6 months	Laboratory procedure
Technetium-99	G/P	HCl or HNO ₃ to pH<2	6 months	Laboratory procedure

Sources:

40 CFR 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants."

APHA/AWWA/WEF, 2012, Standard Methods For the Examination of Water and Wastewater.

ECY 97-602, Analytical Methods for Petroleum Hydrocarbons.

SW-846, Test Methods for Evaluating Solid Waste: Physical/Chemical Methods, Third Edition; Final Update IV-A.

aG = amber glass

aGs = amber glass with septum cap

G = glass

P = plastic

PTFE = polytetrafluorinatedethylene SM = standard method

F.7.1 Sample Preservation

Of the 10,136 groundwater monitoring laboratory samples acquired during CY2013, only 36 samples, or 0.4% of all laboratory samples, were associated with sample preservation issues. Of the 36 samples with sample preservation issues, analyses of only 6 were cancelled. This indicates that incorrect sample preservation is not a major issue for the groundwater monitoring program. Table F.8 lists the preservation issues and the analytes affected for the CY2013 groundwater monitoring effort.

Table F.8. Groundwater Sample Preservation Issues and Dispositions

1 4 5 1 1 1 5 1	Stourist Control of the Control of t											
		Disposition / Number	of Samples Affected	d								
Preservation Issue / Analytes	Report Results	Adjust pH and Report Results	Cancel Analysis	Totals								
Totals	14	16	6	36								
Incorrect pH	1	16	6	23								
IC Anions	_	_	2	2								
Sulfide	_	9	4	13								
ICP Metals	_	1	_	1								
8260 VOCs	1	_	_	1								
Strontium-90	<u> </u>	2	_	2								
Technetium-99	_	4	_	4								
Incorrect temperature	13	-	_	13								
Coliform ^a	1	_	_	1								
Hexavalent Chromium ^a	4	_	_	4								
8260 VOCs ^b	8	_	_	8								

a. For coliform and hexavalent chromium, the *incorrect temperature* preservation issue was for the delivery of samples by Field Sampling Operations to the TestAmerica Richland Laboratory. The samples were delivered within a few hours of sample collection, and the samples did not have time to cool to a storage temperature of ≤6°C prior to delivery of the samples to the analyzing laboratory. Soil and Groundwater Remediation Project personnel deemed as acceptable the results from these samples.

IC = ion chromatography ICP = inductively coupled plasma VOC = volatile organic carbon

F.7.2 Holding Times

Table F.5 summarizes the number of sample results for each analytical method with missed holding times. Of the 133,108 groundwater monitoring laboratory results reported during CY2013, only 109 analytical results, or 0.08% of the groundwater monitoring data set, were affected by missed holding times. This shows improvement over CY2012's 703 analytical results, or 0.5% of the groundwater monitoring data set with missed holding times. Table F.9 lists the reasons for those missed holding times. Most of the samples with missed holding times were often analyzed within two times the holding time; groundwater monitoring project scientists and project coordinators deemed these results acceptable for the groundwater monitoring program. Table F.9 does not include missed holding times for 20 laboratory pH results or for 12 hexavalent chromium results. The analysis holding time for pH is "as soon as possible" and was interpreted to be 24 hours for the purpose of assigning a quantitative holding time; however, the

b. For the 8260 VOCs *incorrect temperature* preservation issue, a laboratory sample storage refrigerator suffered a temperature excursion to 13°C.

laboratories were not held to this 24-hour holding time. The 12 hexavalent chromium results were part of a study in which the hexavalent chromium concentrations for two separate groundwater sample sets were determined once a week over a six-week period to determine how stable the hexavalent chromium concentrations were with time.

Of the 77 remaining analytical results with missed holding times, 36 were for nitrate, nitrite, and phosphate (48-hour holding time), 19 were for hexavalent chromium (24-hour holding time), 12 were for mercury (28-day holding time), eight for total organic carbon (TOC) (28-day holding time), one was for alkalinity (14-day holding time), and one for chloride (28-day holding time). By laboratory, GEL reported eight results with missed holding times, TARL with 17, TASL with 30, and WSCF with 22.

Table F.9. Missed Sample Holding Time Issues

Missed Holding Time Issue	Number of Results*	Percentage of All Missed Holding Times
Totals	77	100.0%
Late Sample Delivery (Other)	33	42.9%
Other Laboratory Issue	23	29.9%
Dilution / Reanalysis	8	10.4%
Late Sample Delivery (Weather)	6	7.8%
Late Sample Delivery (Diverted)	5	6.5%
Sample Reprep / Reanalysis	2	2.6%

^{*}Does not include 20 laboratory pH or 12 hexavalent chromium results with holding time flags.

An explanation of the holding time issues follows:

- Late Sample Delivery (Other): This missed holding time reason covers late delivery of a sample for analysis for miscellaneous issues. This issue affected 17 hexavalent chromium results, eight nitrate results, and eight nitrite results.
- Other laboratory issue: This issue covers miscellaneous reasons for missed holding times such as
 laboratory waste generation issues, laboratory personnel turnover, or laboratory failure to observe
 the holding time limits for samples. Of the 23 results affected by this issue, 12 results were for
 mercury, 6 results for TOC, and one each for alkalinity, hexavalent chromium, nitrate, nitrite, and
 phosphate.
- *Dilution / Reanalysis*: When an analyte exceeded the calibration range during analysis, the sample was diluted and reanalyzed after the holding time lapsed. This issue affected eight samples with six results for nitrate, one for chloride, and one hexavalent chromium result.
- Late Sample Delivery (Weather): This missed holding time reason covers late delivery of a sample for weather-related issues. This issue affected three nitrate results and three nitrite results.
- Late Sample Delivery (Diverted): This missed holding time reason covers late delivery of a sample for analysis because it was diverted from the primary laboratory. This reason was specific to the 48-hour hold time analytes nitrate, nitrite, and phosphate for two groundwater samples acquired on January 23, 2013, and diverted from WSCF to TASL.
- Sample Reprep / Reanalysis: This issue affected the dissolved organic carbon results for two samples.

F.8 Field Quality Control

This section discusses the CY2013 groundwater monitoring field QC data that exceeded the QC acceptance criteria listed in Table F.1. The types of field QC samples that are evaluated in this section are discussed in Section F.4.2.

F.8.1 Field Blanks

FBs are used to assess potential contamination associated with sampling and laboratory activities. Analytical results for the FBs are assessed against the acceptance limits listed in Table F.1. Overall, the percentage of acceptable FB results evaluated during this reporting period was 98.2% (compared to 98.1% for 2012 and 98% for 2011), indicating little problem with contamination during sampling and analysis.

FB results greater than the acceptance criterion of two times the MDL or MDA are identified as suspected contamination. For the common laboratory contaminants 2-butanone, acetone, methylene chloride, toluene, and phthalate esters, the limit is five times the MDL. Results for samples associated with FBs that are above these criteria are given a review qualifier of Q in the HEIS database to indicate potential contamination issues. Associated samples for blanks are defined in Section F.4.2. Table F.10 presents the FB results that exceeded QC limits and Table F.11 compares out-of-limit FBs with out-of-limit method blanks that were analyzed in the same analytical batch.

Table F.10. Field Blank Results Exceeding Quality Control Limits

Table F.10. Fleid Blank Results Exceeding Quality Control Limits										
Constituent	Blank Type	Number of Results	Number Out of Limits	Percent Out of Limits	Range of QC Limits*	Range of Out-of-Limit Results				
		- Tota	l Field Bla	anks Out =	= 250					
General Chemical Parameters: Total Out = 8										
Alkalinity	FTB	57	1	1.8	$280 - 2,000 \ \mu g/L$	2,500 μg/L				
Total dissolved solids	FTB	9	3	33.3	20,000 μg/L	21,000 – 28,000 μg/L				
Total organic carbon	FTB	71	1	1.4	200 μg/L	520 μg/L				
Total organic halides	FTB	50	3	6.0	10 μg/L	10.6 - 19.7 μg/L				
Ammonia and Anions: Total Out = 14										
Chloride	EB	37	1	2.7	240 μg/L	264 μg/L				
Chloride	FTB	94	1	1.1	18 - 240 μg/L	272 μg/L				
Nitrate	EB	37	2	5.4	336 - 354 μg/L	358 - 1330 μg/L				
Sulfide	EB	2	2	100.0	166 μg/L	400 - 430 μg/L				
Sulfide	FTB	13	8	61.5	166 - 330 μg/L	170 – 214,000 μg/L				
		Me	etals: Tot	al Out = 1	26					
Aluminum	FTB	33	2	6.1	10 - 40 μg/L	46.5 - 398 μg/L				
Aluminum	EB	27	1	3.7	20 - 40 μg/L	180 μg/L				
Arsenic	FTB	89	2	2.2	0.4 - 88 μg/L	1.13 - 1.48 μg/L				
Barium	EB	72	1	1.4	0.8 - 8 μg/L	0.812 μg/L				
Barium	FTB	151	1	0.7	0.4 - 8 μg/L	1.3 μg/L				
Boron	FTB	25	1	4.0	4 - 12 μg/L	13.2 μg/L				
Boron	EB	23	1	4.3	8 μg/L	30.8 μg/L				

Table F.10. Field Blank Results Exceeding Quality Control Limits

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Constituent	Blank Type	Number of Results	Number Out of Limits	Percent Out of Limits	Range of QC Limits*	Range of Out-of-Limit Results
Calcium	FTB	145	1	0.7	60 - 100 μg/L	62.7 μg/L
Calcium	EB	64	4	6.2	60 - 100 μg/L	67.1 - 111 μg/L
Chromium	EB	72	1	1.4	0.4 - 10 μg/L	4.37 μg/L
Chromium	FTB	151	4	2.6	0.2 - 10 μg/L	0.512 - 17.3 μg/L
Copper	EB	72	5	6.9	0.4 - 8 μg/L	0.426 - 0.648 μg/L
Copper	FTB	154	6	3.9	0.2 - 8 μg/L	0.426 - 2.73 μg/L
Iron	FTB	145	2	1.4	38 - 80 μg/L	40.7 - 104 μg/L
Iron	EB	64	1	1.6	38 - 80 μg/L	187 μg/L
Lead	EB	29	1	3.4	0.2 μg/L	0.204 μg/L
Lead	FTB	44	3	6.8	0.1 - 92 μg/L	0.195 - 0.423 μg/L
Magnesium	EB	64	1	1.6	8 - 120 μg/L	12.8 μg/L
Magnesium	FTB	145	6	4.1	8 - 120 μg/L	8.4 - 18.3 μg/L
Manganese	EB	70	5	7.1	0.4 - 8 μg/L	0.404 - 0.906 μg/L
Manganese	FTB	151	3	2.0	0.2 - 8 μg/L	0.428 - 0.732 μg/L
Molybdenum	EB	27	1	3.7	0.2 μg/L	0.309 μg/L
Molybdenum	FTB	33	1	3.0	0.1 - 12 μg/L	0.158 μg/L
Nickel	FTB	151	2	1.3	0.2 - 20 μg/L	0.65 - 5.81 μg/L
Nickel	EB	68	3	4.4	0.4 - 20 μg/L	0.426 - 2.04 μg/L
Potassium	EB	64	4	6.2	152 - 500 μg/L	203 - 556 μg/L
Potassium	FTB	145	9	6.2	152 - 500 μg/L	236 - 502 μg/L
Silver	EB	72	5	6.9	0.2 - 10 μg/L	0.224 - 8.2 μg/L
Silver	FTB	151	1	0.7	0.1 - 10 μg/L	0.284 μg/L
Sodium	EB	64	14	21.9	20 - 200 μg/L	24.2 - 311 μg/L
Sodium	FTB	145	16	11.0	20 - 200 μg/L	28 - 133 μg/L
Strontium	EB	66	1	1.5	0.4 - 20 μg/L	7.85 µg/L
Strontium	FTB	130	2	1.5	0.2 - 20 μg/L	3.17 - 10.1 μg/L
Tin	FTB	35	2	5.7	0.1 - 180 μg/L	0.408 - 0.439 μg/L
Tin	EB	27	2	7.4	0.2 μg/L	0.23 - 0.352 μg/L
Uranium	FTB	68	1	1.5	0.1 - 0.2 μg/L	0.922 μg/L
Vanadium	EB	68	2	2.9	0.8 - 20 μg/L	1.15 - 1.47 μg/L
Vanadium	FTB	151	5	3.3	0.4 - 20 μg/L	0.51 - 1.44 μg/L
Zinc	EB	68	1	1.5	4 - 10 μg/L	12.1 μg/L
Zinc	FTB	151	2	1.3	2 - 10 μg/L	8.07 - 46.6 μg/L
	Vol	atile Orga	nic Com	ounds: 1	Total Out = 90	
Acetone	FXR	175	1	0.6	1.7 - 25 μg/L	1.9 μg/L
Benzene	FXR	175	1	0.6	0.12 - 2 μg/L	0.15 μg/L
Carbon tetrachloride	FXR	175	4	2.3	0.26 - 2 μg/L	2.3 - 2.6 μg/L

Table F.10. Field Blank Results Exceeding Quality Control Limits

Bla Constituent Typ		Number of Results	Number Out of Limits	Percent Out of Limits	Range of QC Limits*	Range of Out-of-Limit Results					
Methanol	EB	2	1	50.0	200 μg/L	806 μg/L					
Methylene chloride	FTB	33	8	24.2	5 - 50 μg/L	5.2 - 57 μg/L					
Methylene chloride	FXR	175	74	42.3	1.35 - 8 μg/L	1.5 - 46 μg/L					
Trichloroethene	FXR	175	1	0.6	0.5 - 2 μg/L	3.6 μg/L					
Semivolatile Organic Compounds: Total Out = 1											
Naphthalene	FTB	10	1	10.0	1.8 - 2 μg/L	2.8 μg/L					
	Rá	adiochemi	ical Paran	neters: To	otal Out = 11						
Americium-241	EB	1	1	100.0	0.094 pCi/L	0.1 pCi/L					
Gross alpha	FTB	42	1	2.4	1.3 - 8.6 pCi/L	5.4 pCi/L					
Gross beta	FTB	48	2	4.2	4.8 - 7 pCi/L	6.4 - 130 pCi/L					
Selenium-79	EB	2	1	50.0	14.88 - 29.4 pCi/L	29.7 pCi/L					
Selenium-79	FTB	3	1	33.3	20.4 - 29.6 pCi/L	34.5 pCi/L					
Strontium-90	EB	15	1	6.7	1.62 - 3.6 pCi/L	2.1 pCi/L					
Strontium-90	FTB	31	1	3.2	1.92 - 3 pCi/L	2.3 pCi/L					
Technetium-99	FTB	42	1	2.4	11.6 - 19.82 pCi/L	490 pCi/L					
Thorium-228	EB	1	1	100.0	0.1616 pCi/L	0.266 pCi/L					
Thorium-230	FTB	1	1	100.0	0.32 pCi/L	0.753 pCi/L					

^{*}Because method detection limits are specific to the laboratory and may change during the reporting period, the limits are presented as a range. However, each result was evaluated according to the method detection limit in effect at the time the sample was analyzed.

EB = equipment blank

FTB = full trip blank

FXR = field transfer blank

QC = Quality control.

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Table F.11. Out-of-Limit Field Blanks Compared with Out-of-Limit Method Blanks

Table F.11. Out-of-Limit Field Blanks Compared with Out-of-Limit Method Blanks											
Sample Number	Sample Date	Well Name	FB Type	Constituent	Lab	Method	Analysis Batch Number	Field Blank Result	Method Blank Result		FB Lab Qualifier*
				General Che	mical Pa	arameters					
B2P3C6	5/29/2013	299-W14-13	FTB	Total dissolved solids	WSCF	2540C_TDS	218019	21,000	17,000	μg/L	В
				Ammon	ia and A	nions					
B2N609	1/23/2013	699-40-62	FTB	Sulfide	TASL	9034_SULFIDE	29578	1,100	920	μg/L	C
B2NK50	3/4/2013	699-35-66A	FTB	Sulfide	TASL	9034_SULFIDE	39056	400	600	μg/L	BC
B2NK61	3/4/2013	699-36-66B	EB	Sulfide	TASL	9034_SULFIDE	39056	400	600	μg/L	BC
B2P3F2	4/11/2013	699-38-70B	EB	Sulfide	TASL	9034_SULFIDE	46439	430	234	μg/L	BC
B2PX72	9/30/2013	699-36-70A	FTB	Sulfide	TASL	9034_SULFIDE	76658	270	266	μg/L	BC
					Metals						
B2NB60	2/6/2013	299-W10-27	FTB	Aluminum	WSCF	200.8_METALS_ICPMS	214480	398	5.72	μg/L	D
B2PRX6	7/29/2013	699-45-69C	FTB	Chromium	WSCF	200.8_METALS_ICPMS	219582	0.53	0.16	μg/L	BDC
B2PX74	9/30/2013	699-36-70A	FTB	Chromium	WSCF	200.8_METALS_ICPMS	221993	17.3	0.22	μg/L	D
B2P3C6	5/29/2013	299-W14-13	FTB	Copper	WSCF	200.8_METALS_ICPMS	218214	0.43	0.11	μg/L	BDC
B2P8D5	6/5/2013	299-W22-72	FTB	Copper	WSCF	200.8_METALS_ICPMS	218424	0.61	0.23	μg/L	BDC
B2T1F0	11/25/2013	C7647	FTB	Iron	WSCF	6010_METALS_ICP	224140	104	49.4	μg/L	С
B2NK03	2/14/2013	199-N-46	EB	Magnesium	WSCF	6010_METALS_ICP	213999	12.8	61.8	μg/L	BC
B2NM90	2/19/2013	299-E17-12	FTB	Magnesium	WSCF	6010_METALS_ICP	213999	9.6	61.8	μg/L	BC
B2R6W5	11/6/2013	199-D4-96	FTB	Potassium	WSCF	6010_METALS_ICP	223072	331	415	μg/L	BC
B2R6W8	11/6/2013	199-D4-96	FTB	Potassium	WSCF	6010_METALS_ICP	223072	318	415	μg/L	BC
B2R6X2	11/6/2013	199-D5-104	FTB	Potassium	WSCF	6010_METALS_ICP	223072	325	415	μg/L	BC
B2RVX4	11/12/2013	699-78-62	EB	Potassium	WSCF	6010_METALS_ICP	223431	203	242	μg/L	BC
B2R717	11/14/2013	699-12-2C	FTB	Potassium	WSCF	6010_METALS_ICP	223503	241	160	μg/L	BC
B2T1D7	11/25/2013	C7647	FTB	Potassium	WSCF	6010_METALS_ICP	224140	319	404	μg/L	BC
B2T1F0	11/25/2013	C7647	FTB	Potassium	WSCF	6010_METALS_ICP	224140	279	404	μg/L	BC
B2T1C3	12/2/2013	DD-44-4	FTB	Potassium	WSCF	6010_METALS_ICP	224661	236	327	μg/L	BC

Table F.11. Out-of-Limit Field Blanks Compared with Out-of-Limit Method Blanks

Table F.11. Out-of-Limit Field Blanks Compared with Out-of-Limit Method Blanks											
Sample Number	Sample Date	Well Name	FB Type	Constituent	Lab	Method	Analysis Batch Number	Field Blank Result	Method Blank Result		FB Lab Qualifier*
B2TPB2	12/6/2013	199-N-188	EB	Potassium	WSCF	6010_METALS_ICP	224917	366	448	μg/L	BC
B2TKK4	12/10/2013	299-E27-155	EB	Potassium	WSCF	6010_METALS_ICP	225102	556	1,200	μg/L	BC
B2TKF0	12/13/2013	199-H4-13	FTB	Potassium	WSCF	6010_METALS_ICP	225809	502	648	μg/L	BC
B2NJY5	2/14/2013	199-N-46	EB	Sodium	WSCF	6010_METALS_ICP	213999	35.3	426	μg/L	BC
B2NK03	2/14/2013	199-N-46	EB	Sodium	WSCF	6010_METALS_ICP	213999	61.4	426	μg/L	С
B2NM90	2/19/2013	299-E17-12	FTB	Sodium	WSCF	6010_METALS_ICP	213999	65.2	426	μg/L	С
B2R6W5	11/6/2013	199-D4-96	FTB	Sodium	WSCF	6010_METALS_ICP	223072	84.5	110	μg/L	С
B2R6W8	11/6/2013	199-D4-96	FTB	Sodium	WSCF	6010_METALS_ICP	223072	112	110	μg/L	С
B2R6X2	11/6/2013	199-D5-104	FTB	Sodium	WSCF	6010_METALS_ICP	223072	91.1	110	μg/L	С
B2RVY0	11/12/2013	699-78-62	EB	Sodium	WSCF	6010_METALS_ICP	223404	83.0	103	μg/L	С
B2RVX4	11/12/2013	699-78-62	EB	Sodium	WSCF	6010_METALS_ICP	223431	94.3	76.7	μg/L	С
B2R715	11/14/2013	699-12-2C	FTB	Sodium	WSCF	6010_METALS_ICP	223503	62.3	110	μg/L	BC
B2R717	11/14/2013	699-12-2C	FTB	Sodium	WSCF	6010_METALS_ICP	223503	79.5	110	μg/L	С
B2R718	11/14/2013	699-13-2D	EB	Sodium	WSCF	6010_METALS_ICP	223503	99.0	110	μg/L	С
B2R720	11/14/2013	699-13-2D	EB	Sodium	WSCF	6010_METALS_ICP	223503	79.4	110	μg/L	С
B2RPT6	11/15/2013	199-D2-11	EB	Sodium	WSCF	6010_METALS_ICP	223503	68.6	110	μg/L	BC
B2RPT2	11/15/2013	199-D2-11	EB	Sodium	WSCF	6010_METALS_ICP	223504	64.6	58.4	μg/L	BC
B2RPX3	11/15/2013	199-D5-133	EB	Sodium	WSCF	6010_METALS_ICP	223504	51.9	58.4	μg/L	BC
B2RPX7	11/15/2013	199-D5-133	EB	Sodium	WSCF	6010_METALS_ICP	223504	80.9	58.4	μg/L	С
B2RR21	11/15/2013	199-D5-34	FTB	Sodium	WSCF	6010_METALS_ICP	223504	79.4	58.4	μg/L	С
B2RR25	11/15/2013	199-D5-34	FTB	Sodium	WSCF	6010_METALS_ICP	223504	88.8	58.4	μg/L	C
B2T1D7	11/25/2013	C7647	FTB	Sodium	WSCF	6010_METALS_ICP	224140	133	151	μg/L	C
B2T1F0	11/25/2013	C7647	FTB	Sodium	WSCF	6010_METALS_ICP	224140	128	151	μg/L	С
B2T1C3	12/2/2013	DD-44-4	FTB	Sodium	WSCF	6010_METALS_ICP	224661	89.4	165	μg/L	С
B2TPB2	12/6/2013	199-N-188	EB	Sodium	WSCF	6010_METALS_ICP	224917	311	174	μg/L	С
B2TKK4	12/10/2013	299-E27-155	EB	Sodium	WSCF	6010_METALS_ICP	225102	201	232	μg/L	BC

Table F.11. **Out-of-Limit Field Blanks Compared with Out-of-Limit Method Blanks**

Sample Number	Sample Date	Well Name	FB Type	Constituent	Lab	Method	Analysis Batch Number	Field Blank Result	Method Blank Result	Units	FB Lab Qualifier*
B2NB60	2/6/2013	299-W10-27	FTB	Strontium	WSCF	200.8_METALS_ICPMS	214480	10.1	0.13	μg/L	D
B2N611	1/23/2013	699-40-62	FTB	Vanadium	WSCF	200.8_METALS_ICPMS	213349	0.51	0.50	μg/L	ВС
B2NK52	3/4/2013	699-35-66A	FTB	Vanadium	WSCF	200.8_METALS_ICPMS	215383	0.81	0.63	μg/L	BDC
B2NK63	3/4/2013	699-36-66B	EB	Vanadium	WSCF	200.8_METALS_ICPMS	216717	1.15	0.41	μg/L	BDC
B2P3F4	4/11/2013	699-38-70B	EB	Vanadium	WSCF	200.8_METALS_ICPMS	216717	1.47	0.41	μg/L	BDC
B2P3C6	5/29/2013	299-W14-13	FTB	Vanadium	WSCF	200.8_METALS_ICPMS	218214	1.44	0.50	μg/L	BDC
B2P8D5	6/5/2013	299-W22-72	FTB	Vanadium	WSCF	200.8_METALS_ICPMS	218424	1.21	0.24	μg/L	BDC
B2PRX6	7/29/2013	699-45-69C	FTB	Vanadium	WSCF	200.8_METALS_ICPMS	219582	0.85	0.21	μg/L	BDC
	-	-		Volatile Org	anic Co	mpounds					
				Semivolatile C	rganic (Compounds					
B2MWV0	1/14/2013	N116mArray-1A	FTB	Naphthalene	TASL	8310_SVOA_HPLC	29897	2.80	2.86	μg/L	JOB
	-			Radiochen	nical Par	rameters	_				_

^{*} See Table F.3 for the explanation of the laboratory data quality flags.

EB = equipment blank

FB = field blank

FTB = full trip blank

FXR = field transfer blank

QC = Quality control

TASL = TestAmerica Richland laboratory WSCF = Waste Sampling and Characterization Facility

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The remainder of the FB discussion in this section provides additional context for the information in Tables F.10 and F.11.

For CY2013, 358 FB sets were obtained consisting of 814 samples that were analyzed to generate 13,598 sample results of which 250 (1.8%) exceeded QC limits. By blank type, 49 EB sets were acquired consisting of 163 EB samples; these samples yielded 2,793 results of which 97.7% met the acceptance criteria. For FTBs, 133 blank sets were acquired consisting of 475 samples that yielded 6,517 analytical results of which 98.4% met the acceptance criteria. For FXRs, 176 blank samples yielded 4,288 analytical results of which 98.1% met the acceptance criteria.

By compound class, the 304 general chemical parameter FB results yielded eight results (2.6%) that exceeded QC limits, including one alkalinity, three total dissolved solids, one TOC, and three TOX measurements. Of the 746 ammonia/anion results, 14 (1.9%) exceeded QC limits, including two chloride, two nitrate, and 10 sulfide results.

Of the 4,728 FB metals results for CY2013, 126 (2.7%) exceeded QC limits. Sodium was the worst offender with 30 results exceeding the acceptance criterion followed by potassium (13 results), and copper (11 results). The remaining 72 out-of-limit results were scattered among 16 other metals. Three blank samples (B2R6Y4, B2NB60, and B2TPB2) had at least five metal analytes that exceeded the acceptance criterion. FBs with out-of-limits metal results are frequently the result of a mix-up between the actual blank sample and a groundwater sample either in the field or in the laboratory.

CY2013 groundwater monitoring FBs yielded 5,955 VOC results. Of these results, 90 (1.5%) exceeded QC limits and included 82 methylene chloride results. The remaining VOC analytes and the number of results out of limits were acetone (1), benzene (1), carbon tetrachloride (4), methanol (1), and trichloroethene (1). During CY2012, a study of VOC contamination in groundwater FBs determined that the deionized water used to generate the FBs is the most likely source of the methylene chloride and to a lesser extent, carbon tetrachloride and chloroform found in the FBs (SGW-52194). The same study also concluded that the appearance of acetone, bromomethane, carbon disulfide, chloromethane, tetrachloroethene, and toluene in laboratory method blanks indicates that these volatile organic analytes may be introduced as contaminants during laboratory sample preparation and analysis and may appear as spurious analytes in groundwater samples. Corrective actions to decrease the appearance of spurious organic compounds in groundwater monitoring FBs and samples have been initiated, but are yet to be completed.

Of the 1,227 SVOC results, only one result (0.1%) for naphthalene exceeded QC limits. Of the 638 radiochemical parameter results, 11 (1.7%) exceeded QC limits. The 11 out-of-limit results were distributed over eight radiochemical parameters.

Table F.11 compares out-of-limit FB results with out-of-limit MB results. The majority of the table entries show that the FB and MB results are similar in value; in some instances the MB value is significantly greater than the FB value. For most the FBs in Table F.11, the source of FB contamination is more likely caused by laboratory sample handling and preparation and is not the result of sample bottle preparation and sample collection activities. The ICP metals provide most of the entries in Table F.11 with potassium and sodium being the most common metal contaminants; 27 of the FB metals entries in Table F.11 are from just five analytical batches.

F.8.2 Field Duplicate Samples

Field duplicate samples are replicate groundwater samples sent to the same laboratory and are used to assess field sampling and laboratory measurement precision. According to Table F.1, the results of field duplicates must have a precision less than or equal to 20% as measured by the RPD (Equation F-1). Field

duplicates with at least one result greater than five times the MDL or MDA were evaluated. Field duplicate results that have an RPD greater than 20% are given a review qualifier of Q in the HEIS *RESULT* table to indicate potential precision issues. Field duplicate values with a review qualifier of Y were included in the assessment of duplicate precision.

For CY2013, 170 duplicate sample sets were acquired consisting of 691 sample pairs. These 691 sample pairs yielded 9,642 pairs of results of which 2,629 result pairs (27.3%) met the evaluation criterion. Of these 2,629 result pairs, 2,503 (95.2%) were acceptable, indicating reasonable field sampling and intra-laboratory precision. Table F.12 presents the duplicate results that exceeded QC limits. For comparison, the CY2012 percentage of acceptable duplicate results was 94.2%, and the CY2011 percentage of acceptable duplicate results was 95%.

Table F.12. Field Duplicates Exceeding Quality Control Limits

Table F.12. Field Duplicates Exceeding Quality Control Limits						
Constituent	Laboratory	Number of Duplicates	Number of Duplicates Evaluated ^a	Number Out of Limits ^b	Percent Out of Limits	Range of Out- of-Limit RPD ^c
Total Field Duplicate Results Out = 126						
General Chemical Parameters: Total Out = 3						
Alkalinity	GEL	1	1	1	100	70.9
Coliform Bacteria	TARL	2	1	1	100	23.2
Dissolved organic carbon	WSCF	3	2	1	50.0	36.9
Ammonia and Anions: Total Out = 12						
Bromide	WSCF	20	1	1	100	181.3
Cyanide	WSCF	15	9	4	44.4	24.6 - 46.6
Fluoride	WSCF	126	37	2	5.4	28.1 - 28.6
Nitrate	WSCF	126	123	2	1.6	93.7 - 138.8
Sulfide	TASL	14	4	3	75.0	140 - 162.4
Metals: Total Out = 91						
Aluminum	WSCF	68	9	5	55.6	43.7 - 144.1
Arsenic	WSCF	131	72	5	6.9	22.5 - 110.2
Barium	WSCF	238	226	3	1.3	26.7 - 39.1
Boron	WSCF	33	14	3	21.4	20.4 - 129.6
Chromium	WSCF	238	105	13	12.4	21.2 - 133.8
Cobalt	WSCF	242	6	5	83.3	128.9 - 171.8
Copper	WSCF	242	20	13	65.0	23.8 - 182.7
Iron	WSCF	193	36	7	19.4	49.4 - 133.1
Lead	WSCF	91	7	4	57.1	29 - 159.2
Manganese	WSCF	211	30	12	40.0	20.9 - 190.6
Molybdenum	WSCF	71	61	4	6.6	21.1 - 147.7
Nickel	WSCF	209	20	3	15.0	21 - 120.4
Potassium	WSCF	193	193	1	0.5	28.7
Strontium	WSCF	195	191	1	0.5	25.9
Tin	WSCF	74	2	2	100	35.7 - 143.6
Uranium	WSCF	73	71	2	2.8	31.6 - 168

Table F.12. Field Duplicates Exceeding Quality Control Limits

Constituent	Laboratory	Number of Duplicates	Number of Duplicates Evaluated ^a	Number Out of Limits ^b	Percent Out of Limits	Range of Out- of-Limit RPD ^c			
Vanadium	WSCF	209	55	4	7.3	24.8 - 116.9			
Zinc	WSCF	209	4	4	100	55.6 - 195.6			
Volatile Organic Compounds: Total Out = 1									
Methylene chloride	WSCF	42	1	1	100	169.2			
Semivolatile Organic Compounds: Total Out = 1									
Methyl methanesulfonate	WSCF	10	1	1	100	198.9			
	Radio	ochemical Par	ameters: Tota	ol Out = 18					
Carbon-14	TARL	22	12	2	16.7	21.3 - 63.1			
Gross alpha	WSCF	46	2	2	100	23 - 23.5			
Gross beta	WSCF	61	46	8	17.4	20.9 - 100			
Iodine-129	TARL	26	10	2	20.0	24.7 - 29.4			
Selenium-79	TARL	2	1	1	100	23.3			
Strontium-90	WSCF	45	21	1	4.8	26.4			
Technetium-99	WSCF	61	39	1	2.6	65			
Uranium-238	WSCF	2	2	1	50.0	25			

a. Duplicates with at least one result five times greater than the method detection limit or minimum detectable activity were evaluated.

RPD = Relative Percent Difference

GEL = GEL Laboratory

TARL = TestAmerica Richland Laboratory

TASL = TestAmerica St. Louis

WSCF = Waste Sampling and Characterization Facility

Metals had the largest number of duplicate result failures with 91 data pairs exceeding the RPD criterion of 20%. Historically, many of the out-of-limit duplicates for metals were attributed to unfiltered samples in which suspended solids in the samples tend to cause discrepancies between result pairs. However, for CY2013, the metals duplicate result failures occurred in almost as many filtered samples as unfiltered samples. This may indicate possible sample swaps either in the field or in the laboratory, a sample contamination event that affected one of the duplicate pair but not the other, or a dilution error during sample preparation.

b. Duplicate control limit is a relative percent difference less than or equal to 20%.

c. In cases where a non-detected result was compared with a measured value, the method detection limit or minimum detectable activity was used for the non-detected concentration.

Four sample duplicates with the most RPD failures are briefly discussed below.

- B2RR39 / B2RR40: These non-filtered duplicates were acquired from well 199-D5-97 on 11/25/2013 and were analyzed for 200.8 metals at WSCF on 12/16/2013. Seven metals (arsenic, barium, chromium, molybdenum, strontium, uranium, and vanadium) had RPDs that exceeded the RPD limit of 20% and ranged from 25.9% to 147.7%. The metal concentrations of sample B2RR39 were more representative of the historical trend for the source well; sample B2RR40 tended to have lower concentrations of the metal analytes than its sibling sample. It is possible that differences in particulate concentrations between the two samples are responsible for the differences in metals concentrations, but dilution errors during sample preparation cannot be ruled out.
- B2RRX5 / B2RTJ9: These filtered duplicates were acquired from well 199-K-124A on 11/22/2013 and were analyzed for 200.8 metals at WSCF on 12/16/2013. Seven metals (arsenic, chromium, lead, manganese, uranium, vanadium, and zinc) had RPDs that exceeded the RPD limit of 20% and ranged from 36.9% to 195.6%. After examination of the data, the metals results for sample B2RTJ9 are more representative of the historical trends for well 199-K-19 which was also sampled on 11/22/2013. Furthermore, the metals results for sample B2RVH2 from well 199-K-19 are more representative of well 199-K-124A. Therefore, the most likely explanation for the poor agreement of the 200.8 results between samples B2RRX5 and B2RTJ9 is a swap of B2RTJ9 with a sample from well 199-K-19. A request for data review has been initiated to rerun the 200.8 analysis of both B2RTJ9 and B2RVH2 to determine whether the sample swap occurred in the field or in the laboratory.
- B2NWF3 / B2NWF4: These non-filtered duplicates were acquired from well C7641 on 4/3/2013 and were analyzed at WSCF for 200.8 metals on 4/30/2013 and for 6010 metals on 4/11/2013. Four 200.8 metals (aluminum, chromium, copper, and molybdenum) and one 6010 metal (iron) had RPDs that exceeded the RPD limit of 20% and ranged from 37.3% to 139.7%. Good agreement exists between the two samples for the alkali metals and alkaline earth metals so the lack of agreement for the five metals is most likely due to differences in the unfiltered particulates between the two samples.
- B2RFM0 / B2RFM1: These non-filtered duplicates were acquired from well C7643 on 9/16/2013 and were analyzed at WSCF for 200.8 metals on 9/26/2013 and for 6010 metals on 9/24/2013. Four 200.8 metals (aluminum, chromium, manganese, and molybdenum) and one 6010 metal (iron) had RPDs that exceeded the RPD limit of 20% and ranged from 27.1% to 145.2%. Good agreement exists between the two samples for the alkali metals and alkaline earth metals so the lack of agreement for the five metals is most likely due to differences in the unfiltered particulates between the two samples.

F.8.3 Quadruplicate Total Organic Carbon and Total Organic Halides Samples

TOC and TOX are classified as RCRA indicator analytes, and the samples for these analytes are usually taken in quadruplicate (40 CFR 265.92). For these analytes, the %RSD of the quadruplicate results was determined as described in Section F.4.2 and compared to a precision limit of 20%. Field quadruplicate sample results are evaluated only if at least one result is at least five times the laboratory MDL.

For TOC, 196 quadruplicate sample sets were taken. Of these 196 sample sets, 84 sets (42.9%) met the evaluation criterion and of these, 74 sets (88.1%) had %RSDs less than 20%. This represents reasonable reproducibility for TOC samples. The %RSD values of the 10 TOC quadruplicate result sets that exceeded 20% ranged from 22.0% to 177%. Table F.13 presents the quadruplicate sample sets that

exceeded QC limits. One possible explanation for these failures may be inconsistent removal of inorganic carbon (typically present as bicarbonate or carbonate) from the sample prior to the determination of organic carbon in the sample. If inorganic carbon is not consistently and completely removed from the sample before determining organic carbon, the apparent concentration of organic carbon is likely to vary across a set of quadruplicate samples.

For TOX, 176 quadruplicate sample sets were taken. Of these 176 sample sets, only three sets (1.7%) met the evaluation criterion and of these, two (66.7%) exceeded the 20% RSD criterion. One possible explanation for these failures may be inconsistent rinsing of inorganic chloride from the sample prior to the determination of organic halides in the sample. If inorganic chloride is not consistently and completely removed from the sample before determining organic halides, the apparent concentration of organic halides is likely to vary across a set of quadruplicate samples.

Table F.13. Total Organic Carbon and Total Organic Halide Quadruplicate Results Exceeding Quality Control Limits.

Quality Control Limits.											
Well Name	Lab	RL μg/L	Resul µg/l		Resu µg/		Resu µg/		Resu µg/	_	%RSD*
Total Organic Carbon: Total Out = 10											
199-N-57	WSCF	100	885	_	458	_	453		474	_	37.3
299-E32-3	WSCF	100	645	_	492	_	778	_	509	_	22.0
299-E32-5	WSCF	100	599	_	414	_	533	_	301	_	28.5
299-E32-6	WSCF	100	192	В	542	_	529		591	_	39.5
299-E33-266	WSCF	100	755	_	464	_	465	_	436	_	28.4
299-E33-28	WSCF	100	304	_	525	_	530	_	578	_	25.3
299-E33-29	WSCF	100	227	В	502	_	500	_	192	В	47.6
299-E33-34	WSCF	100	343	_	608	_	629	_	623	_	25.2
299-E34-8	WSCF	100	1,180	_	218	В	242	В	444	_	86.5
299-W10-30	WSCF	100	7,220	_	229	В	216	В	247	В	176.7
	Total Organic Halides: Total Out = 2										
299-E25-48	WSCF	5	47	X	5	U	80	X	5	U	106.3
299-W10-30	WSCF	5	21	_	17	_	26	_	16	_	23.6

^{*}The percent RSD was compared to the field duplicate relative percent difference limit of 20%.

Laboratory qualifier flags:

B = (WSCF) analyte detected between the reporting limit and the estimated quantitation limit

U = analyte not detected above the reporting limit

X = (WSCF TOX) greater than 10% breakthrough detected between first and second adsorption columns

RL = reporting limit

%RSD = percent relative standard deviation

WSCF= Waste Sampling and Characterization Facility

F.8.4 Field Split Samples

Field split samples are duplicate samples that are sent to two different laboratories to allow interlaboratory comparisons of analytical results. These interlaboratory comparisons are used to evaluate the performance of the laboratories, to determine the extent of any analytical problems, and to confirm out-of-trend results. According to Table F.1, the precision acceptance criterion for field splits is an RPD less than or equal to 20%. Only those field split results pairs with at least one result greater than five times the MDLs or MDAs of both laboratories were evaluated. If the laboratory reported an estimated quantitation limit instead of an MDL, the evaluation criterion was one times the estimated quantitation limit instead of five times the MDL. For TOC and TOX split samples, a matching set of quadruplicate samples was submitted to each of the two laboratories. To evaluate the interlaboratory reproducibility for TOC and TOX, an average result was first calculated for each laboratory's quadruplicate sample set, and then the average values from the two laboratories were used to calculate the RPD.

For CY2013, 75 field split sample sets consisting of 309 sample pairs yielded 3,588 pairs of field split data. Of the 3,588 data pairs, 726 pairs (20.2%) met the evaluation criterion. For the evaluated field splits, 630 pairs (86.8%) met the 20% RPD criterion. For comparison, the percentage of pairs within the limit was 86.4% for CY2012 and 84% for CY2011. Table F.14 summarizes the results for field splits that exceeded the 20% RPD limit.

Table F.14. Field Splits Exceeding Quality Control Limits

	_	cia opiito Exo	<u> </u>						
Constituent	Total Number of Splits	Number of Splits Evaluated ^a	Number Out of Limits	Percent Out of Limits	Range of Out-of-Limit Relative Percent Difference ^b				
Total Field Split Results Out = 96									
	1		meters: Total (ı					
Alkalinity	15	15	1	6.7	197.8				
	Amn	nonia and Anio	ns: Total Out =	: 13					
Fluoride	45	17	13	76.5	21.8 - 58.3				
Metals: Total Out = 65									
Aluminum	34	5	5	100	123.3 - 178.6				
Barium	93	92	3	3.3	21 - 167.6				
Boron	13	5	5	100	92.7 - 154.1				
Calcium	60	60	2	3.3	199.6 - 199.7				
Chromium	93	19	8	42.1	30.2 - 196.7				
Cobalt	93	2	2	100	44.2 - 152.8				
Copper	93	5	5	100	27.3 - 170.4				
Iron	60	10	10	100	28.0 - 174				
Lead	36	1	1	100	40.0				
Magnesium	60	60	2	3.3	197.7				
Manganese	68	9	6	66.7	21.4 - 184.5				
Molybdenum	36	10	2	20.0	21.4 - 41.0				
Nickel	64	3	1	33.3	104.2				
Silver	93	2	2	100	148.7 - 151.8				
Sodium	60	60	2	3.3	196.9 - 198.1				

Table F.14. Field Splits Exceeding Quality Control Limits

Constituent	Total Number of Splits	Number of Splits Evaluated ^a	Number Out	Percent Out of Limits	Range of Out-of-Limit Relative Percent Difference ^b				
Strontium	61	61	2	3.3	189.5 - 189.9				
Tin	31	2	2	100	193.2 - 194.4				
Uranium	30	24	2	8.3	20.6 - 32.6				
Zinc	64	9	3	33.3	21.9 - 83.1				
Volatile Organic Compounds: Total Out = 4									
Trichloroethene	21	6	4	66.7	27.9 - 153.5				
	Semivolat	ile Organic Co	mpounds: Tota	l Out = 0					
	Radioc	hemical Param	eters: Total Ou	ıt = 13					
Carbon-14	16	7	3	42.9	21.4 - 96.2				
Gross beta	23	11	2	18.2	27.0 - 88.9				
Strontium-90	33	12	1	8.3	20.6				
Technetium-99	27	1	1	100	183.9				
Tritium	36	21	6	28.6	25.0 - 115.8				

a. Splits sample results were evaluated when at least one result was greater than five times the method detection limit or minimum detectable activity of both laboratories. In cases where a non-detected result was compared with a measured value, the method detection limit or minimum detectable activity was used as the non-detected result.

b. Split control limit is a relative percent difference less than or equal to 20%.

The metals analyses constituted 67.7% of the total split failures. The majority of these failures occurred on unfiltered samples; hence, the variability of suspended solids in the samples is a likely cause of discrepancies in the results for non-filtered samples. Other possible causes for the discrepancies are samples swapped either in the field or in the laboratory and possible dilution errors at the time of analysis. As one example, the split sample pair with the most metals failures was B2P304 (TASL) and B2P305 (WSCF); both samples were unfiltered. The eight metals with RPD failures and their associated RPDs were: aluminum (147%), chromium (70.4%), cobalt (44.2%), copper (50.0%), iron (82.0%), lead (40.0%), and molybdenum (41.0%). However, the results for the alkali metals and alkaline earths for this split pair were quite comparable. This indicates that the RPD failures between these two samples are most likely caused by differences in the number and composition of the unfiltered particulates in the two samples.

After the metals analyses, the ammonia/anions and radiochemical results each accounted for 13.5% of the split sample failures. All 13 of the anion split failures were for fluoride with 11 failures between WSCF and TASL, one between WSCF and GEL, and one between TASL and GEL. TASL uniformly reported fluoride levels greater than WSCF with RPDs ranging between 21.8% and 48.6%. This bias was apparent for groundwater sample fluoride concentrations less than about 500 μ g/L. An examination of the fluoride results for the blind standards did not reveal any strong bias in fluoride results among the laboratories when the fluoride concentration was greater than about 3,000 μ g/L. At a blind standard concentration of 1,300 μ g/L fluoride, GEL had an average recovery of 102%, TASL of 93.4%, and WSCF of 87.1%.

For the radiochemical parameters, the majority of the splits failures were posted for tritium (six), carbon-14 (three), and gross beta (two); strontium-90 and technetium-99 posted one failure each. The six tritium

failures were between TARL and WSCF and did not show any consistent bias between the two laboratories. The three carbon-14 failures between GEL and TARL showed TARL reporting lower activities with respect to GEL. A low bias in the TARL carbon-14 results has been observed historically, but the laboratory addressed this issue with changes to its carbon-14 sample preparation procedure. Only two quarters of carbon-14 blind standards data exist that allow comparison between GEL and TARL; no obvious pattern of bias was observed between the two laboratories. Likewise for the two gross beta splits between TARL and WSCF with out-of-limit RPDs: no particular bias was discerned between the gross beta results.

For the two remaining analyte classes, VOCs had four split pair failures, or 4.2% of the total failures. The four failures were for trichloroethene and were between TASL and WSCF; no consistent bias was detected between the two laboratories. No split pair results passed the evaluation criterion for the semivolatile organic compounds.

F.9 Laboratory Quality Control

This Section Fiscusses the CY2013 groundwater monitoring laboratory batch QC data that exceeded the QC acceptance criteria listed in Table F.1. The types of laboratory QC samples that are evaluated in this section are discussed in Section F.4.3. Table F.15 summarizes the laboratory QC data by laboratory, and Table F.16 summarizes the laboratory QC data by analyte class. Overall, the laboratory QC data indicate that laboratory analytical measurements for the groundwater monitoring program are produced within the QC limits of Table F.1. Of the 73,495 laboratory batch QC measurements reported with groundwater monitoring results, 98.5% of the measurements met the groundwater monitoring QC requirements; this is comparable to the 99.0% reported for CY2012. When the laboratories detect failures in batch QC samples, the laboratories usually apply a QC laboratory qualifier to the data as noted in Table F.3.

 Table F.15.
 Laboratory Quality Control Results by Laboratory

	Table L.IJ.	Laboratory &	danty Control	Tesuits by Lab			
QC Parameter	222-S	Eberline	GEL	TestAmerica Richland	TestAmerica St. Louis	WSCF	Total
Total Laboratory QC Results	77	10	2,865	1,190	11,775	57,572	73,489
Laboratory QC Results Out	4	0	43	19	206	842	1,114
Laboratory QC Results Out Percent	5.2	0.0	1.5	1.6	1.7	1.5	1.5
Method Blanks Total	27	3	567	562	2,169	15,557	18,885
Method Blanks Out	4	0	7	8	70	269	358
Method Blanks Out Percent	14.8	0.0	1.2	1.4	3.2	1.7	1.9
Lab Control Samples Total	27	3	588	354	2,809	11,131	14,912
Lab Control Samples Out Low	0	0	0	0	3	54	57
Lab Control Samples Out High	0	0	1	1	17	7	26
Lab Control Samples Out Percent	0.0	0.0	0.2	0.3	0.7	0.5	0.6
Lab Control Sample Duplicates Total	_	_	28	_	810	22	860
Lab Control Sample Duplicates Out	_	_	0	_	2	6	8
Lab Control Sample Duplicates Out Percent	_	_	0.0	_	0.2	27.3	0.9
Matrix Spikes Total	13	3	920	118	3,143	15,418	19,615
Matrix Spikes Out Low	0	0	21	2	23	190	236
Matrix Spikes Out High	0	0	8	1	42	141	192
Matrix Spikes Out Percent	0.0	0.0	3.2	2.5	2.1	2.1	2.2
Matrix Spike Duplicates Total	1	_	404	40	1,454	7,479	9,378
Matrix Spike Duplicates Out	0	_	3	0	18	64	85
Matrix Spike Duplicates Out Percent	0.0	_	0.7	0.0	1.2	0.9	0.9
Sample Duplicates Total	9	1	75	116	166	1,136	1,503
Sample Duplicates Out	0	0	3	7	3	19	32
Sample Duplicates Out Percent	0.0	0.0	4.0	6.0	1.8	1.7	2.1
Surrogates Total	_	_	275	_	1,224	6,202	7,701
Surrogates Out Low	_	_	0	_	6	36	42
Surrogates Out High	_	_	0	_	22	25	47
Surrogates Out Percent	_	_	0.0	_	2.3	1.0	1.2
Surrogate Duplicates Total	_	_	8	_		627	635
Surrogate Duplicates Out	_	_	0	_	_	31	31
Surrogate Duplicates Out Percent	_	_	0.0	_	_	4.9	4.9

Table F.16. Laboratory Quality Control Results by Analyte Class

	Table F. To.	16. Laboratory Quality Control Results by Analyte Class						
QC Parameter	General Chemical Parameters	Ammonia / Anions	Metals	Volatile Organic Compounds	Semivolatile Organic Compounds	Radiochemical Parameters	Total	
Total Laboratory QC Results	2,347	9,803	26,092	18,966	12,764	3,517	73,489	
Laboratory QC Results Out	53	178	390	230	206	57	1,114	
Laboratory QC Results Out Percent	2.3	1.8	1.5	1.2	1.6	1.6	1.5	
Method Blanks Total	299	2,141	6,353	4,774	3,438	1,880	18,885	
Method Blanks Out	30	19	275	1	21	12	358	
Method Blanks Out Percent	10.0	0.9	4.3	0.0	0.6	0.6	1.9	
Lab Control Samples Total	543	2,152	6,376	2,894	1,887	1,060	14,912	
Lab Control Samples Out Low	0	0	6	4	31	16	57	
Lab Control Samples Out High	0	1	6	5	12	2	26	
Lab Control Samples Out Percent	0.0	0.0	0.2	0.3	2.3	1.7	0.6	
Lab Control Sample Duplicates Total	_	_	28	533	299	_	860	
Lab Control Sample Duplicates Out	_	_	0	2	6	_	8	
Lab Control Sample Duplicates Out Percent	_	_	0.0	0.4	2.0	_	0.9	
Matrix Spikes Total	718	3,186	8,872	4,126	2,460	253	19,615	
Matrix Spikes Out Low	6	99	55	36	39	1	236	
Matrix Spikes Out High	2	53	37	95	5	0	192	
Matrix Spikes Out Percent	1.1	4.8	1.0	3.2	1.8	0.4	2.2	
Matrix Spike Duplicates Total	343	1,460	4,273	2,063	1,230	9	9,378	
Matrix Spike Duplicates Out	5	3	11	38	26	2	85	
Matrix Spike Duplicates Out Percent	1.5	0.2	0.3	1.8	2.1	22.2	0.9	
Sample Duplicates Total	133	864	190	_	1	315	1,503	
Sample Duplicates Out	5	3	0	_	0	24	32	
Sample Duplicates Out Percent	3.8	0.3	0.0	_	0.0	7.6	2.1	
Surrogates Total	264	_	_	4,284	3,153	_	7,701	

 Table F.16.
 Laboratory Quality Control Results by Analyte Class

QC Parameter	General Chemical Parameters	Ammonia / Anions	Metals	Volatile Organic Compounds	Semivolatile Organic Compounds	Radiochemical Parameters	Total
Surrogates Out Low	3		_	4	35	_	42
Surrogates Out High	0	_	_	43	4	_	47
Surrogates Out Percent	1.1	_	_	1.1	1.2	_	1.2
Surrogate Duplicates Total	47	_	_	292	296	_	635
Surrogate Duplicates Out	2	_	_	2	27	_	31
Surrogate Duplicates Out Percent	4.3	_	_	0.7	9.1	_	4.9

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F.9.1 Laboratory Method Blanks

Laboratory MBs are used to assess potential contamination associated with laboratory sample preparation and analysis. Of the 18,885 laboratory MB results evaluated for CY2013, 98.1% met the QC criteria outlined in Table F.1 indicating little problem with laboratory contamination. This is slightly poorer than the 98.5% reported for CY2012 and the 99.5% reported for CY2011.

Evaluation of MB results was based on the MB QC limits listed in Table F.1. For the common laboratory contaminants 2-butanone, acetone, methylene chloride, phthalate esters, and toluene, the QC limit is five times the MDL. The laboratories flag results associated with out-of-limit blank results in the laboratory qualifier field in the HEIS database as described in Table F.3. For inorganic analytes (including the indicator analytes TOC and TOX), results associated with an out-of-limit MB are flagged with a C. For organic analytes, results associated with an out-of-limit MB are flagged with a B. The laboratory may not flag the groundwater sample result if the analyte concentration in the method blank is less than 5% of the concentration of the analyte in a groundwater sample analyzed in the same batch. Table F.17 summarizes the CY2013 out-of-limit MB results.

Table F.17. Method Blank Out-of-Limit Results

Table F.17. Method Blank Out-of-Limit Results									
Constituent	Laboratory	Number of Results	Number Out of Limits	Percent Out of Limits	Range of QC Limits ^a	Range of Out-of- Limit Results			
		Total Me	ethod Bla	nks Out =	: 358				
General Chemical Parameters: Total Out = 30									
Alkalinity	TASL	9	6	66.7	140 - 540 μg/L	150 - 600 μg/L			
Dissolved organic carbon	WSCF	8	3	37.5	45 μg/L	47.9 - 270 μg/L			
Specific Conductance	TASL	2	2	100.0	0.097 uS/cm	0.23 - 0.6 uS/cm			
Total dissolved solids	GEL	1	1	100.0	3,400 µg/L	7,140 µg/L			
Total dissolved solids	WSCF	27	5	18.5	10,000 μg/L	11,000 - 29,000 μg/L			
Total organic carbon	TASL	9	3	33.3	270 μg/L	572 - 703 μg/L			
Total organic carbon	WSCF	88	9	10.2	45 μg/L	45.1 - 88.9 μg/L			
Total organic halides	TASL	8	1	12.5	1.8 μg/L	3.62 μg/L			
	Ai	mmonia a	nd Anion	s: Total (
Chloride	TASL	35	2	5.7	20 μg/L	31.1 - 70.8 μg/L			
Cyanide	TASL	9	6	66.7	1.5 μg/L	1.65 - 7.34 μg/L			
Sulfate	222-S	5	3	60.0	13 μg/L	59 - 66 μg/L			
Sulfide	TASL	31	8	25.8	83 μg/L	134 - 920 μg/L			
		Meta	als: Total	Out = 27	5				
Aluminum	WSCF	110	4	3.6	5 - 12 μg/L	5.58 - 8.88 μg/L			
Antimony	TASL	25	1	4.0	1.7 - 4 μg/L	2.45 μg/L			
Arsenic	WSCF	180	7	3.9	0.2 - 44 μg/L	0.204 - 0.306 μg/L			
Barium	WSCF	266	4	1.5	0.2 - 4 μg/L	0.228 - 0.616 μg/L			
Beryllium	TASL	25	1	4.0	0.35 - 0.61 μg/L	2.1 μg/L			
Boron	TASL	15	2	13.3	10 - 10.8 μg/L	11.97 - 26.59 μg/L			
Boron	WSCF	60	3	5.0	0.5 - 20 μg/L	0.61 - 42 μg/L			
Calcium	WSCF	169	10	5.9	30 - 50 μg/L	32.4 - 313 μg/L			

Table F.17. Method Blank Out-of-Limit Results

	Table F.17	. 1010	tiloa Bia	iik Out o	it-Limit Results				
•		Number of	Number Out of	Percent Out of	a	Range of Out-of-			
Chromium	Laboratory WSCF	Results	Limits	Limits	Range of QC Limits ^a	Limit Results			
		266	18	6.8	0.1 - 5 μg/L	0.106 - 2.03 μg/L			
Cobalt	TASL	25	1	4.0	0.22 - 4.9 μg/L	5.1 μg/L			
Copper	TASL	25	1	4.0	0.45 - 4.6 μg/L	0.692 μg/L			
Copper	WSCF	269	17	6.3	0.1 - 4 μg/L	0.109 - 1.45 μg/L			
Hexavalent Chromium	222-S	2	1	50.0	9 μg/L	20.7 μg/L			
Hexavalent Chromium	WSCF	293	1	0.3	2 μg/L	3.8 μg/L			
Iron	GEL	6	2	33.3	30 μg/L	50.7 - 74 μg/L			
Iron	WSCF	169	5	3.0	19 - 40 μg/L	25.2 - 145 μg/L			
Lead	WSCF	123	4	3.3	0.05 - 46 μg/L	0.0508 - 0.0973 μg/L			
Magnesium	WSCF	169	11	6.5	4 - 60 μg/L	4.01 - 61.8 μg/L			
Manganese	WSCF	242	10	4.1	0.1 - 4 μg/L	0.103 - 0.334 μg/L			
Mercury	TASL	4	1	25.0	0.06 μg/L	0.116 μg/L			
Mercury	WSCF	38	1	2.6	0.05 μg/L	0.077 μg/L			
Molybdenum	GEL	5	2	40.0	0.165 μg/L	0.212 - 0.214 μg/L			
Molybdenum	WSCF	115	5	4.3	0.05 - 6 μg/L	0.0631 - 1.03 μg/L			
Nickel	WSCF	237	14	5.9	0.1 - 10 μg/L	0.151 - 9 μg/L			
Potassium	GEL	6	1	16.7	50 μg/L	82.6 μg/L			
Potassium	WSCF	169	38	22.5	76 - 250 μg/L	80.7 - 1200 μg/L			
Silicon	WSCF	4	1	25.0	30 - 33 μg/L	331 μg/L			
Silver	TASL	25	4	16.0	0.05 - 6 μg/L	0.066 - 0.322 μg/L			
Silver	WSCF	267	9	3.4	0.05 - 5 μg/L	0.125 - 5.47 μg/L			
Sodium	WSCF	169	49	29.0	10 - 100 μg/L	10.1 - 426 μg/L			
Strontium	TASL	17	1	5.9	0.06 - 0.54 μg/L	2.3 μg/L			
Strontium	WSCF	222	1	0.5	0.1 - 10 μg/L	0.131 μg/L			
Tin	TASL	13	3	23.1	1 μg/L	1.02 - 2.5 μg/L			
Tin	WSCF	110	3	2.7	0.05 - 90 μg/L	0.0525 - 0.0685 μg/L			
Vanadium	WSCF	237	20	8.4	0.2 - 10 μg/L	0.209 - 5.8 μg/L			
Zinc	TASL	16	5	31.2	5.2 - 8.3 μg/L	5.3 - 9 μg/L			
Zinc	WSCF	237	14	5.9	1 - 5 μg/L	1.18 - 46.3 μg/L			
	Volat	tile Organ	ic Compo	ounds: To	otal Out = 1				
Acetone ^b	TASL	20	1	5.0	1.7 μg/L	1.76 μg/L			
Semivolatile Organic Compounds: Total Out = 21									
Acenaphthene	TASL	19	1	5.3	0.07 - 2 μg/L	0.0922 μg/L			
Anthracene	TASL	19	1	5.3	0.078 - 2 μg/L	0.0814 μg/L			
Benzo(a)anthracene	TASL	19	1	5.3	0.062 - 2 μg/L	0.682 μg/L			
Benzo(a)pyrene	TASL	19	1	5.3	0.106 - 2 μg/L	0.533 μg/L			
Benzo(b)fluoranthene	TASL	19	1	5.3	0.11 - 2 μg/L	0.788 μg/L			

Table F.17. Method Blank Out-of-Limit Results

Constituent	Laboratory	Number of Results	Number Out of Limits	Percent Out of Limits	Range of QC Limits ^a	Range of Out-of- Limit Results
Benzo(ghi)perylene	TASL	19	2	10.5	0.08 - 2 μg/L	0.0892 - 0.295 μg/L
Benzo(k)fluoranthene	TASL	19	1	5.3	0.146 - 2 μg/L	0.241 μg/L
Chrysene	TASL	19	1	5.3	0.078 - 2 μg/L	0.589 μg/L
Fluoranthene	TASL	19	2	10.5	0.068 - 2 μg/L	0.317 - 1.47 μg/L
Fluorene	TASL	19	1	5.3	0.064 - 2 μg/L	0.279 μg/L
Indeno(1,2,3-cd)pyrene	TASL	19	1	5.3	0.08 - 2 μg/L	0.369 μg/L
Naphthalene	TASL	19	2	10.5	0.136 - 2 μg/L	2.8 - 2.86 μg/L
Phenanthrene	TASL	19	4	21.1	0.096 - 2 μg/L	0.104 - 1.74 μg/L
Pyrene	TASL	19	2	10.5	0.074 - 2 μg/L	0.082 - 1.13 μg/L
	Radi	ochemica	al Parame	ters: Tota	al Out = 12	
Carbon-14	TARL	37	2	5.4	30.2 - 47.6 pCi/L	42.8 - 110 pCi/L
Gross beta	TARL	17	1	5.9	3.5 - 3.92 pCi/L	4.22 pCi/L
Gross beta	WSCF	140	1	0.7	0.64 - 34 pCi/L	6.3 pCi/L
Iodine-129	TARL	42	1	2.4	0.284 - 0.622 pCi/L	0.574 pCi/L
Potassium-40	WSCF	68	1	1.5	196 - 940 pCi/L	330 pCi/L
Selenium-79	TARL	3	2	66.7	23 - 25.8 pCi/L	26 - 26.7 pCi/L
Strontium-90	GEL	4	1	25.0	3.62 - 3.94 pCi/L	4.49 pCi/L
Strontium-90	TARL	23	1	4.3	0.726 - 15.94 pCi/L	5.45 pCi/L
Strontium-90	WSCF	116	1	0.9	1.72 - 5 pCi/L	6.1 pCi/L
Tritium	TARL	34	1	2.9	41.6 - 746 pCi/L	952 pCi/L

a. For general chemical parameters, ammonia and anions, metals, and volatile organic compounds, the quality control limit for method blanks is the method detection limit. For semivolatile organic compounds, the quality control limit is twice the method detection limit. For radiochemical constituents, the quality control limit is twice the minimum detectable activity.

b. The quality control limit for this analyte is five times the method detection limit.

222-S = 222-S Laboratory

GEL = GEL Laboratory

TARL = TestAmerica Richland Laboratory

TASL = TestAmerica St. Louis

WSCF = Waste Sampling and Characterization Facility

By laboratory, 222-S reported the lowest success rate for MBs at 85.2%; however, 222-S reported only 0.1% of all groundwater analytical results for CY2013.

TASL had the next lowest success rate of 96.8% for the 2,169 MB results reported by that laboratory. TASL reported 12 general chemical parameter MB failures including six for alkalinity and three for total organic carbon. For the anions, TASL reported 16 MB failures including chloride (two), cyanide (six) and sulfide (eight). For the metals, TASL reported 20 out-of-limit MBs with silver (four), tin (three), and zinc (five) being the most frequently reported failures. TASL reported the only SVOC MB failures with 21

MB results that exceeded QC limits. Eleven of these SVOC MB failures were traced to TASL analytical batch number 95631 and another five traced to analytical batch number 72639. The SVOC with the most frequent MB failure was phenanthrene (four failures) and also one of the highest out-of-limit ratios at 18.1 times the QC limit. Fluoranthene had the highest out-of-limit ratio at 21.6 times the QC limit.

The WSCF laboratory had the next lowest failure rate for MBs at 98.3%. Most of the MB failures were for the ICP metals; those metals with 10 or more MB failures were calcium, chromium, copper, magnesium, manganese, nickel, potassium, sodium, vanadium, and zinc. Of these analytes, 29.0% of the MBs analyzed for sodium failed followed by potassium (22.5%).

The remaining laboratories reported MB success rates greater than 98.5%.

By analyte category, general chemical parameters had the lowest MB success rate at 90.0% with 30 MB failures. Fifteen of these failures were for dissolved/total organic carbon: three at TASL and 12 at WSCF. Metals had the next lowest success rate at 95.7% with 275 failed MBs. Most of these failures are attributable primarily to the ICP metals MB failures at TASL and WSCF. The remaining analyte classes had MB success rates greater than 99%.

F.9.2 Laboratory Control Samples and Laboratory Control Sample Duplicates

Laboratory control sample (LCS) recoveries give a measure of the accuracy of an analytical result, and the LCS duplicate RPD gives a measure of the repeatability of the analytical result. Laboratories may apply a laboratory qualifier of O or X and an accompanying explanatory note when LCS recoveries or laboratory control sample duplicate (LCSD) RPDs are outside QC limits. LCS results were available across all the analyte categories while LCSD results were available primarily for VOCs and SVOCs.

Overall, 99.4% of the percent recoveries for the 14,912 reported LCSs and 99.1% of the RPDs for the 860 reported LCSDs met the QC criteria cited in Table F.1. This is comparable to the acceptance rates of 99.2% for LCS percent recoveries and 99.3% for LCSD RPDs during CY2012 and the acceptance rates of 99% for LCS percent recoveries and 98% for LCSD RPDs during CY2011. These success rates for percent recoveries and RPDs provide assurance that the analytical measurement processes are in good control and are producing results with sufficient accuracy and precision to meet the needs of the groundwater monitoring program. Table F.18 summarizes the CY2013 out-of-limits LCS and LCSD results.

Table F.18. Laboratory Control Sample Out-of-Limit Results

Constituent	Laboratory	Number of LCS ^a		Percent Out of Limit High	_	Percent RPD Out of Limit			
General Chemical Parameters: Recovery Limits = 80% - 120%, RPD Limit = 20%									
Ammonia and Ai	nions: Recovery	<u> Limits = 80</u>	<u>)% - 120%, F</u>	PD Limit = 2	20% ^b				
Phosphate	GEL	1	_	100.0	_	_			
Metals: I	Recovery Limits	= 80% - 120	%, RPD Lim	it = 20% ^b	-	-			
Boron	WSCF	60	1.7	_	_	_			
Selenium	WSCF	115	3.5	_	_	_			
Silver	WSCF	267	_	1.9	_	_			
Tin	WSCF	110	0.9	_	_	_			
Uranium	WSCF	124	_	0.8	_	_			
Volatile Organic Compounds:	Recovery and R	PD Limits =	Laboratory	Specific (St	atistically D	erived)			

 Table F.18.
 Laboratory Control Sample Out-of-Limit Results

TableTite	Laboratory	Onti Or Oan	ipic out or	Lilling IXCOC	1110	
Constituent	Laboratory	Number of LCS ^a	Percent Out of Limit Low	Percent Out of Limit High	Number of LCSD	Percent RPD Out of Limit
1,1,1-Trichloroethane	TASL	37	_	2.7	18	_
1,1-Dichloroethane	TASL	39	_	2.6	19	_
1,1-Dichloroethane	WSCF	94	1.1	_		_
1,1-Dichloroethene	WSCF	94	1.1	_	_	_
2-Butanone	TASL	37	_	_	18	11.1
Carbon disulfide	WSCF	94	1.1	_		_
Ethylbenzene	TASL	39	_	2.6	19	_
trans-1,2-Dichloroethylene	TASL	34	_	2.9	17	_
trans-1,2-Dichloroethylene	WSCF	94	1.1	_	_	_
Trichloroethene	TASL	39	_	2.6	19	_
Semivolatile Organic Compound	s: Recovery and	RPD Limits	s = Laborato	rv Specific (Statistically	Derived)
1,2,4-Trichlorobenzene	WSCF	24		—	1	100
1,4-Dichlorobenzene	WSCF	28	_	_	1	100
1,4-Dioxane	WSCF	27	3.7	_	1	_
2,4-Dichlorophenol	WSCF	34	2.9	_	1	_
2,4-Dimethylphenol	WSCF	30	3.3	_	1	100
2,4-Dinitrotoluene	TASL	2	_	50	_	_
2-Chlorophenol	WSCF	32	3.1	_	1	
2-Methylphenol (cresol, o-)	WSCF	34	2.9	_	1	_
2-Nitrophenol	WSCF	34	2.9	_	1	_
2-Picoline	WSCF	25	12.0	_	1	_
4-Chloro-3-methylphenol	WSCF	32	3.1	_	1	_
4-Nitrophenol	WSCF	32	3.1	_	1	100
Bis(2-chloro-1-methylethyl)ether	TASL	2	_	50	_	_
Bis(2-ethylhexyl) phthalate	WSCF	27	3.7	_	1	_
Dimethoate	WSCF	18	44.4	_	_	_
Endrin aldehyde	TASL	14	7.1	_	5	_
Fluoranthene	TASL	31	_	10	12	_
Fluorene	TASL	31	_	7	12	_
Hexachlorobenzene	TASL	2	_	50	_	_
Hexachlorophene	WSCF	17	5.9	_	_	_
Naphthalene	TASL	31	3.2	7	12	_
Naphthalene	WSCF	27	_	_	1	100
n-Nitrosodimethylamine	WSCF	19	5.3	_	_	_
Pentachlorophenol	WSCF	35	2.9	_	1	100
Phenanthrene	TASL	31	_	7	12	_
Phenol	TASL	8	12.5	_	_	_
Phenol	WSCF	35	2.9	_	1	_
1	1					

Table F.18. Laboratory Control Sample Out-of-Limit Results

Constituent	Laboratory	Number of LCS ^a	Percent Out of Limit Low	Percent Out of Limit High	Number of LCSD	Percent RPD Out of Limit	
Tributyl phosphate	WSCF	25	16.0	_	1	_	
Radiochemical Parameters: Recovery Limits = 70% - 130%, RPD Limit = 20%							
Gross alpha	WSCF	116	8.6	_	_	_	
Gross beta	WSCF	140	4.3	_	_	_	
Strontium-90	TARL	23	_	4.3	_	_	
Technetium-99	WSCF	63	_	1.6	_	_	

a. Includes both laboratory control samples and laboratory control sample duplicates.

LCS = laboratory control sample

LCSD = laboratory control sample duplicate

RPD = relative percent difference

GEL = GEL Laboratory

TARL = TestAmerica Richland Laboratory TASL = TestAmerica St. Louis Laboratory

WSCF = Waste Sampling and Characterization Facility

For all six reporting laboratories, greater than 99% of their LCS recoveries met QC recovery criteria. For the LCSDs, WSCF met the RPD QC requirement for only 72.7% of that laboratory's LCSD results. However, this represents only six of 22 LCSD results; all six failures were for the LCSD in WSCF 8270 SVOC batch 216080. Two other laboratories reported LCSD data: of the 28 LCSD results GEL reported, 100% met RPD requirements, and of the 810 LCSD results TASL reported, 99.8% met RPD requirements. These LCS and LCSD results indicate sufficient method control, analytical accuracy, and analytical repeatability to meet the data needs for the groundwater monitoring program.

F.9.3 Matrix Spikes and Matrix Spike Duplicates

Matrix spikes provide a measure of the accuracy of an analytical result and are used to determine if sample matrix effects may have affected analytical results. MSDs give a measure of the repeatability of the analytical result. Only those samples that were spiked at a level at least one-fourth of the sample concentration were evaluated. For MS recovery failures, the laboratories apply a laboratory qualifier of N for non-gas chromatography – mass spectrometry methods, and a laboratory qualifier of T for gas chromatography – mass spectrometry methods. MS and MSD results were available across all the analyte categories although the MSD RPD data for the radiochemical parameters are limited to gross alpha and gross beta analyses from GEL. In this discussion, the set of MS recoveries also includes recoveries for MSDs.

Of the 20,242 MS results reported for CY2013, 19,615 (96.9%) met the evaluation criterion. Of the 19,615 evaluated MS results, 97.8% met the percent recovery QC criteria cited in Table F.1. Of the 9,676 MS/MSD pairs reported, 9,378 (96.9%) met the evaluation criterion; of the 9,378 evaluated pairs, 99.1% met the RPD QC criteria of Table F.1. These success rates for percent recoveries and RPDs are similar to those for the LCS and LCSD QC and provide additional assurance that the laboratories are producing data with sufficient accuracy and precision to meet the needs of the groundwater monitoring program. By comparison, 99.2% of the percent recoveries and 99.4% of the RPDs met QC criteria in CY2012, and

b. Laboratory-specific limits were used if provided. Otherwise the stated limits were used to evaluate LCS/LCSDs.

98.5% of the percent recoveries and 97.9% of the RPDs met QC criteria in CY2011. Table F.19 summarizes the CY2013 out-of-limits MS and MSD results.

Table F.19. Matrix Spike Out-of-Limit Results

Table F.19. Matrix Spike Out-of-Limit Results							
Constituent	Laboratory	Number of MS ^a	Percent Out of Limit Low	Percent Out of Limit High	Number of MSD	Percent RPD Out of Limit	
General Chemistry Parameters: Recovery Limits = 75% - 125%, RPD Limit = 20% ^b							
Total organic carbon	WSCF	292	0.7	_	146	_	
Total organic halides	TASL	8	12.5	_	_	_	
Total organic halides	WSCF	272	0.4	_	136	1.5	
Total petroleum hydrocarbons - diesel range	WSCF	50	2.0	4.0	25	8.0	
Total petroleum hydrocarbons - gasoline range	WSCF	22	4.5	_	11	9.1	
Ammonia and A	nions: Recovery	/ Limits = 75	5% - 125%, F	RPD Limit = 2	20% ^b		
Bromide	WSCF	68	_	1.5	34	_	
Chloride	GEL	8	_	37.5	_	_	
Chloride	WSCF	558	8.2	4.7	279	0.4	
Cyanide	GEL	4	25.0	_	_	_	
Cyanide	WSCF	44	6.8	2.3	22	4.5	
Fluoride	GEL	7	_	14.3		_	
Fluoride	TASL	37	_	2.7	2	_	
Fluoride	WSCF	608	0.8	0.3	304	0.3	
Nitrate	GEL	8	_	12.5	_	_	
Nitrate	WSCF	540	2.6	1.1	270	_	
Nitrite	GEL	7	14.3	_	_	_	
Nitrite	TASL	36	5.6	_	2	_	
Nitrite	WSCF	610	0.2	0.2	305	_	
Phosphate	TASL	2	50.0	_	_	_	
Phosphate	WSCF	104	1.9	1.0	52	_	
Sulfate	GEL	7	_	42.9	_	_	
Sulfate	TASL	36	_	2.8	2	_	
Sulfate	WSCF	340	6.8	1.5	170	_	
Metals:	- Recovery Limits	= 75% - 125	%, RPD Lim	it = 20% ^b			
Aluminum	GEL	8	37.5	_	3	_	
Aluminum	WSCF	122	0.8	_	61	_	
Antimony	WSCF	358	_	0.6	179	_	
Arsenic	WSCF	206	_	0.5	103	_	
Barium	GEL	15	13.3	_	6	_	
Barium	WSCF	358	1.1	_	179	_	
Beryllium	WSCF	322	_	_	161	0.6	
Boron	TASL	30	_	13.3	15	_	

 Table F.19.
 Matrix Spike Out-of-Limit Results

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Constituent	Laboratory	Number of MS ^a	Percent Out of Limit Low	Percent Out of Limit High	Number of MSD	Percent RPD Out of Limit
Boron	WSCF	72	1.4	_	36	2.8
Cadmium	WSCF	360	0.3	0.3	180	_
Calcium	TASL	20	_	10.0	10	_
Calcium	WSCF	272	1.5	0.4	136	0.7
Chromium	WSCF	368	0.5	_	184	0.5
Cobalt	WSCF	374	0.5	_	187	_
Copper	WSCF	362	0.6	_	181	0.6
Hexavalent Chromium	WSCF	280	2.1	2.1	_	_
Iron	WSCF	334	_	0.6	167	0.6
Lead	WSCF	146	0.7	_	73	_
Magnesium	WSCF	324	0.3	0.3	162	0.6
Manganese	WSCF	330	0.6	_	165	_
Molybdenum	WSCF	124	_	2.4	62	_
Nickel	WSCF	320	0.6	_	160	_
Selenium	WSCF	132	0.8	0.8	66	1.5
Silver	TASL	50	2.0	_	25	_
Silver	WSCF	344	3.5	0.9	172	0.6
Sodium	WSCF	296	0.7	0.3	148	_
Strontium	WSCF	294	_	0.7	147	_
Tin	WSCF	110	_	1.8	55	_
Uranium	TARL	9	11.1	11.1	_	_
Uranium	WSCF	162	0.6	1.9	81	_
Vanadium	WSCF	318	0.3	_	159	_
Zinc	WSCF	320	0.6	0.3	160	1.2
Volatile Organic Compounds:	Recovery and R	PD Limits =	Laboratory	Specific (St	atistically D	erived)
1,1,1-Trichloroethane	TASL	42	_	2.4	21	_
1,1,1-Trichloroethane	WSCF	172	0.6	2.3	86	2.3
1,1,2,2-Tetrachloroethane	WSCF	36	_	13.9	18	_
1,1,2-Trichloroethane	WSCF	172	_	1.7	86	2.3
1,1-Dichloroethane	TASL	42	_	4.8	21	_
1,1-Dichloroethane	WSCF	172	2.3	2.3	86	4.7
1,1-Dichloroethene	TASL	42	_	2.4	21	_
1,1-Dichloroethene	WSCF	182	1.1	3.8	91	1.1
1,2-Dichloroethane	TASL	42	_	4.8	21	_
1,2-Dichloroethane	WSCF	172	_	1.2	86	2.3
1,2-Dichloropropane	WSCF	36	5.6	2.8	18	_
1,4-Dioxane	TASL	28	_	_	14	14.3
1-Butanol	TASL	36		_	18	22.2

Table F.19. Matrix Spike Out-of-Limit Results

Constituent Laboratory Number of MSa Percent Out of Limit Low Percent Out of Limit High Number of MSD Percent RPD Out of Limit High 2-Butanone GEL 22 13.6 — 11 — 2-Butanone TASL 42 — 9.5 21 9.5 4-Methyl-2-pentanone TASL 42 — — 21 4.8 Acetone GEL 22 45.5 — 11 — Acetone TASL 42 4.8 — 21 4.8 Benzene TASL 42 — 4.8 21 — Benzene WSCF 182 0.5 0.5 91 2.2 Bromodichloromethane WSCF 36 — 5.6 18 —
2-Butanone GEL 22 13.6 — 11 — 2-Butanone TASL 42 — 9.5 21 9.5 4-Methyl-2-pentanone TASL 42 — — 21 4.8 Acetone GEL 22 45.5 — 11 — Acetone TASL 42 4.8 — 21 4.8 Benzene TASL 42 — 4.8 21 — Benzene WSCF 182 0.5 0.5 91 2.2
4-Methyl-2-pentanone TASL 42 — — 21 4.8 Acetone GEL 22 45.5 — 11 — Acetone TASL 42 4.8 — 21 4.8 Benzene TASL 42 — 4.8 21 — Benzene WSCF 182 0.5 0.5 91 2.2
Acetone GEL 22 45.5 — 11 — Acetone TASL 42 4.8 — 21 4.8 Benzene TASL 42 — 4.8 21 — Benzene WSCF 182 0.5 0.5 91 2.2
Acetone TASL 42 4.8 — 21 4.8 Benzene TASL 42 — 4.8 21 — Benzene WSCF 182 0.5 0.5 91 2.2
Benzene TASL 42 — 4.8 21 — Benzene WSCF 182 0.5 0.5 91 2.2
Benzene WSCF 182 0.5 0.5 91 2.2
Bromodichloromethane WSCF 36 _ 56 19
Diomodelioronicularic wiscr 30 - 3.0 10 -
Bromoform WSCF 36 — 13.9 18 5.6
Carbon disulfide WSCF 172 4.1 1.7 86 1.2
Carbon tetrachloride GEL 22 4.5 — 11 —
Carbon tetrachloride TASL 38 — 5.3 19 —
Chlorobenzene WSCF 182 — 0.5 91 2.2
Chloroform TASL 38 2.6 5.3 19 —
cis-1,2-Dichloroethylene TASL 36 — 5.6 18 —
cis-1,2-Dichloroethylene WSCF 162 — 1.9 81 1.2
Dibromochloromethane WSCF 36 — 8.3 18 5.6
Diethyl ether WSCF 4 — 50.0 2 —
Ethyl cyanide TASL 36 — 5.6 18 5.6
Ethylbenzene TASL 42 — 4.8 21 —
Ethylbenzene WSCF 168 — 1.2 84 1.2
Methylene chloride TASL 42 — 4.8 21 —
Styrene WSCF 36 5.6 8.3 18 5.6
Tetrachloroethene TASL 40 — 7.5 20 —
Tetrahydrofuran TASL 36 — — 18 11.1
Toluene WSCF 182 — 1.6 91 1.1
trans-1,2-Dichloroethylene TASL 36 — 2.8 18 —
trans-1,2-Dichloroethylene WSCF 150 — 4.7 75 1.3
trans-1,3-Dichloropropene WSCF 36 — 5.6 18 5.6
Trichloroethene TASL 40 — 7.5 20 —
Trichloroethene WSCF 188 — 0.5 94 1.1
Semivolatile Organic Compounds: Recovery and RPD Limits = Laboratory Specific (Statistically Derived)
1,4-Dioxane WSCF 44 4.5 — 22 4.5
2-Picoline WSCF 40 15.0 — 20 15.0
4-Nitrophenol WSCF 58 — 1.7 29 20.7
Acenaphthylene TASL 14 7.1 — 7 —
Benzo(a)pyrene TASL 14 14.3 — 7 —
Benzo(b)fluoranthene TASL 14 14.3 — 7 —

Table F.19. Matrix Spike Out-of-Limit Results

Constituent	Laboratory	Number of MS ^a	Percent Out of Limit Low	Percent Out of Limit High	Number of MSD	Percent RPD Out of Limit	
Benzo(ghi)perylene	TASL	14	14.3	_	7	_	
Benzo(k)fluoranthene	TASL	14	14.3	_	7	14.3	
Bis(2-chloro-1-methylethyl)ether	TASL	4	_	50.0	2	_	
Bis(2-ethylhexyl) phthalate	WSCF	44	4.5	_	22	_	
Dibenz[a,h]anthracene	TASL	14	14.3	_	7	14.3	
Dimethoate	WSCF	34	29.4	_	17	_	
Endrin aldehyde	TASL	8	12.5	_	4	50.0	
Hexachlorobenzene	TASL	4	_	25.0	2	_	
Hexachlorophene	WSCF	34	_	_	17	11.8	
Indeno(1,2,3-cd)pyrene	TASL	14	14.3	_	7	_	
Naphthalene	GEL	2	_	_	1	100	
Naphthalene	TASL	14	7.1	_	7	_	
n-Nitrosodimethylamine	WSCF	34	5.9	_	17	_	
Pentachlorophenol	WSCF	64	_	_	32	9.4	
Phenanthrene	TASL	14	_	_	7	14.3	
Phenol	WSCF	64	_	_	32	15.6	
Pyrene	WSCF	42	_	2.4	21	_	
Tributyl phosphate	Tributyl phosphate WSCF 40 5.0 — 20 —						
Radiochemical Analytes: Recovery Limits = 60% - 140%, RPD Limit = 20% b							
Gross alpha	GEL	8	_	_	4	50.0	
Technetium-99	TARL	29	3.4	_		_	

a. Includes both matrix spike and matrix spike duplicates.

MS/MSD = matrix spike / matrix spike duplicate

RPD = relative percent difference

GEL = GEL Laboratory

TARL = TestAmerica Richland

TASL = TestAmerica St. Louis

WSCF = Waste Sampling and Characterization Facility

By laboratory, GEL reported the lowest rate for MS recoveries at 96.8%. Percentage-wise, 20.0% (10 results) of the GEL MS/MSD recoveries for anions were outside of QC limits, and eight of these were high recoveries for the ion chromatographic (IC) anions chloride (three results), fluoride (one), nitrate (one), and sulfate (three). The GEL IC anion recovery limits were 90% to 110%; the high recoveries ranged from 111% to 131%. GEL had a 2.7% failure rate (14 results) for the VOCs; all failed low. Three of the failures were for 2-butanone and 10 for acetone. Both of these compounds are polar and the low spike recoveries may indicate a matrix effect for the associated samples or loss of these polar compounds to active sites during chromatography. GEL reported five low MS recoveries for ICP-MS metals: three for aluminum and two for barium. The low recoveries ranged from 55.6% to 73.2% with a lower QC limit of

b. Laboratory-specific limits were used if provided. Otherwise the stated limits were used to evaluate MS/MSDs.

75%. GEL reported only three MS/MSD RPD failures: one for naphthalene and two for gross alpha. The three failed RPDs ranged from 21% to 23%, only slightly greater than the RPD limit of 20%.

The laboratory with the next lowest MS recovery rate was TARL at 97.5%. However, this only represents a total of three MS recovery failures: two of nine determinations of total uranium by kinetic phosphorescence analysis (50.9% and 208.5% recoveries) and one of 29 technetium-99 determinations (44.1% recovery). Of their 40 evaluated MSD results, TARL had no RPDs that exceeded QC limits.

TASL and WSCF both reported MS recovery success rates of 97.9%. By analyte category, TASL's lowest MS recovery success rate was 96.9% for VOCs: of 1,082 evaluated MS recoveries, three were low and 31 were high. Two of the low recoveries were for acetone; however, acetone contamination was reported in the method blank associated with these recoveries and may indicate the acetone detected in the parent samples was due to contamination during sample handling. Such contamination of the parent samples would lead to apparent low MS acetone recoveries. The 31 high recoveries ranged from 116% to 148% and were distributed over a variety of both polar and non-polar VOCs. In most cases these recoveries are only a few percentage points greater than the laboratory's statistically derived upper limits for MS recoveries for VOCs. While the occurrence of these high recoveries may indicate a slight high bias in TASL VOC results, these high results represent only 2.9% of the MS data for TASL VOCs. In comparison, the TASL VOC LCS recovery failures were all high but only represent 0.5% of the LCS data. Of the 541 MSD RPDs evaluated, 13 exceeded the RPD limit of 20%: out-of-limit recoveries ranged from 21% to 47% with the majority of out-of-limit results only slightly greater than 20%. Almost all the out-of-limit RPDs were associated with polar analytes including 1,4-dioxane, 1-butanol, 2-butanone, and tetrahydrofuran. These polar compounds tend to be more difficult to separate from their aqueous matrix and will readily interact with active sites during VOC analysis. These effects may lead to poorer RPDs for these compounds.

TASL's next lowest MS recovery success rate was 97.7% for SVOCs. Of the 782 SVOC MS recoveries evaluated, 15 were low and three were high. All but three of the out-of-limit SVOC results were determined by EPA method 8270, and most of these were polynuclear aromatic hydrocarbons. This is in contrast with TASL's LCS recoveries for SVOCs: the majority of the out-of-limit LCS recoveries were high. The disparity between the LCS and MS recoveries may indicate a possible matrix effect with the groundwater or an occasional deficient spike of the MS samples. Of the 391 MSD RPDs evaluated, five exceeded the RPD limit of 20%: out-of-limit recoveries ranged from 21% to 128% with the majority of out-of-limit results only slightly greater than 20%. Three of the out-of-limit RPDs were associated with polynuclear aromatic hydrocarbons; the other two were for two determinations of endrin aldehyde.

TASL returned 97.8% success rates for MS recoveries and no MSD RPD failures for both general chemical parameters and anions. For the metals, TASL reported a 99.3% success rate for MS recoveries and no MSD RPD failures.

Similarly to TASL, WSCF reported an overall 97.9% success rate for MS recoveries. Unlike TASL, WSCF's lowest performance was in the anions category with a success rate of 95.3% for MS recoveries. The large majority of the MS/MSD failures were for the ion-chromatography anions with about two low failures for every high failure. Of the IC anions, chloride, nitrate, and sulfate exhibited the poorest MS recoveries. For cyanide, the low recovery failure rate was 6.8% and the high recovery failure rate was 2.3%. The MSD RPD failure rate for WSCF anions was only 0.2%.

After the anions, WSCF's next lowest MS recovery rate was for the VOCs. Overall, WSCF reported a 96.7% success rate for VOC MSs: of the 2,530 MS results that met the evaluation criterion, 83 results were outside the recovery criteria with 19 (0.8%) failing low and 64 (2.5%) failing high. Almost all the failures were for non-polar compounds. The recovery behavior of the MS results does not mirror that of the LCS

results and may indicate an occasional slight high bias in WSCF's preparation of VOC MS samples. Of the 1,265 MSD results that met the evaluation criteria, 25 (2.0%) had RPDs greater than the limit of 20%; the out-of-limit RPDs ranged from 21.2% to 104%.

After the VOCs, WSCF reported MS recovery success rates of 98.4% for the SVOCs. Of the 1,606 SVOC MS results that met the evaluation criteria, 24 recoveries (1.5%) were less than the lower recovery limits and two recoveries (0.1%) were greater than the upper recovery limits. Two compounds, 2-picoline and dimethoate, accounted for the majority of the low recoveries with six and 10 low recoveries each. The recovery behavior for the SVOC MSs mirrors that of the LCS recoveries; this may indicate a slight low bias for the WSCF SVOC results. Of the 803 MSD RPD results that met evaluation criteria, 20 RPDs were greater than the 20% RPD limit; the out-of-limit RPDs ranged from 20.1% to 200%. The SVOC analyte 2-picoline is associated with three 200% RPDs and also had MS recoveries near 0%. The LCS results for 2-picoline also show low recoveries; this likely indicates severe loss of this Lewis base during sample preparation and chromatography.

For the general chemical parameters, WSCF reported a 98.9% MS recovery success rate; of the 662 MS results that met the evaluation criteria, seven results fell outside the recovery criteria. Four analytes had out-of-limit MS/MSD recoveries: total organic carbon (292 results, two low recoveries), total organic halides (272 results, one low recovery), total petroleum hydrocarbons – diesel range (50 results, one low recovery, two high recoveries), and total petroleum hydrocarbons – gasoline range (22 results, one low recovery). Three analytes also had MSD RPDs that exceeded the 20% RPD criterion: total organic halides (136 RPD results, two exceeded limits), total petroleum hydrocarbons – diesel range (25 RPD results, two exceeded limits), and total petroleum hydrocarbons – gasoline range (11 RPD results, one exceeded limits). For these same analytes, WSCF reported no LCS failures. Consequently, no consistent bias is apparent for the results WSCF reported for these general chemical parameters.

WSCF reported no MS failures for the radiochemical parameters.

By analyte class, the highest MS out-of-limit recovery rates were: anions at 4.8%, VOCs at 3.2%, and SVOCs at 1.8%. The general chemical parameters had a 1.1% out-of-limit recovery rate; all but one TASL MS result for total organic halides are discussed previously in the WSCF MS section. Radiochemical parameters had an out-of-limit rate of only 0.4%. The rates of MSDs that exceeded RPD limits were: radiochemical parameters at 22.2% (this represents only two of nine total reported MSDs for radiochemical parameters), SVOCs at 2.1%, VOCs at 1.8%, and general chemical parameters at 1.5%. Ammonia/anions and metals had rates of out-of-limit MSD RPDs at less than 1%.

For the anions, 3,186 MS results were evaluated with 152 results outside the recovery limits; GEL, TASL, and WSCF reported these results. The MS failures occurred for all the ion-chromatography anions and cyanide; two-thirds of the MS failures were low recoveries. Chloride had the highest out-of-limit recovery rate at 12.4% (605 MS results evaluated with 46 failing low and 29 high); most of these results were generated at WSCF. Cyanide had the next highest out-of-limit recovery rate at 8.8% (57 MS results evaluated with four failing low and one high) followed by sulfate at 8.3% (385 MS results evaluated with 23 failing low and nine high). For the anion MSDs, only one out-of-limit RPD each was reported for chloride, cyanide, and fluoride.

For the VOCs, 4,126 MSs met the evaluation criteria with 36 MS recoveries less than the lower recovery limits and 95 results greater than the upper recovery limits. GEL, TASL, and WSCF reported all the VOC MS results. The out-of-limit MS results were distributed over 28 polar and non-polar VOC analytes. For the VOC MSDs, 2,063 MSD results were evaluated; of these, 38 exceeded the 20% RPD criterion. The MSD failures were reported by TASL and WSCF and were distributed over 24 polar and non-polar compounds. The out-of-limit RPD values ranged from 21.0% to 104%.

For the SVOCs, 2,460 MSs met the evaluation criteria with 39 MS recoveries less than the lower recovery limits and five recoveries greater than the upper recovery limits. GEL, TASL, and WSCF reported all the SVOC MS results. The MS failures were distributed over 20 polar and non-polar SVOC analytes. For the SVOC MSDs, 1,230 MSD results were evaluated; of these, 26 exceeded the 20% RPD criterion. The MSD failures were reported by GEL, TASL, and WSCF and were distributed over 11 polar and non-polar compounds. The out-of-limit RPD values ranged from 20.1% to 200%; 2-picoline had three reported MSDs at 200% and is discussed previously with the WSCF SVOC MS results.

F.9.4 Laboratory Sample Duplicates

Laboratory sample duplicates give a measure of the repeatability of an analytical result. Only those sample results with values five times greater than the MDL or the MDA, or one times the estimated quantitation limit were evaluated. The RPDs for sample duplicates that met the evaluation criteria were compared to either the laboratory-specific statistically derived RPD maximum or to a maximum of 20% if no laboratory-specific RPD was available. When laboratory sample duplicate RPDs are outside QC limits, laboratories may apply a laboratory qualifier of X and an accompanying explanatory note.

Of the 3,773 reported laboratory sample duplicates, 1,503 (39.8%) met the evaluation criterion; of these, 32 RPDs exceeded the precision criteria for an overall acceptance rate of 97.9%. This acceptance rate, while not as high as those for the LCSD (99.1%) and MSD (99.1%) quoted in the previous sections, still demonstrates reasonable analytical reproducibility. The WSCF Laboratory reported most of the sample duplicate data, and 222-S, GEL, Eberline, TARL, and TASL reported the remainder. By analyte class, laboratory sample duplicate data were reported for the general chemical parameters, anions, metals, and the radiochemical parameters; WSCF reported a single sample duplicate result for the SVOCs (Aroclor-1254) that met the RPD criterion. For the radiochemical parameters, the laboratory sample duplicate is the primary measure of analytical precision although some MSD RPD data do exist for gross alpha and gross beta results from GEL. Table F.20 summarizes the out-of-limit results for laboratory sample duplicates.

Table F.20. Laboratory Sample Duplicate Out-of-Limit Results

Constituent	Laboratory	Number of Laboratory Duplicates	Number Laboratory Duplicates Evaluated*	Percent RPD Out of Limit	Range of RPD Out			
	General Chem	ical Parameters:	RPD Limit = 20	%				
Coliform Bacteria	TARL	9	3	100.0	31.3 - 102.4			
Total organic carbon	TASL	8	3	33.3	26.0			
Total organic halides	GEL	4	2	50.0	23.4			
	Ammonia and Anions: RPD Limit = 20%							
Cyanide	GEL	4	2	50.0	25.8			
Cyanide	TASL	9	5	20.0	58.0			
Sulfide	TASL	32	8	12.5	92.0			
	Ме	tals: RPD Limit	= 20%					
	Volatile Organ	ic Compounds:	RPD Limit = 20%	6				
	Semivolatile Org	anic Compound	s: RPD Limit = 2	20%				
Radiochemical Parameters: RPD Limit = 20%								
Gross alpha	WSCF	116	9	33.3	22.4 - 60.2			
Gross beta	WSCF	139	67	14.9	22.2 - 112.6			

Table F.20. Laboratory Sample Duplicate Out-of-Limit Results

Constituent	Laboratory	Number of Laboratory Duplicates	Number Laboratory Duplicates Evaluated*	Percent RPD Out of Limit	Range of RPD Out
Iodine-129	GEL	4	2	50.0	20.3
Iodine-129	TARL	39	19	21.1	26.7 - 54.4
Plutonium-239/240	WSCF	17	5	20.0	24.8
Uranium-233/234	WSCF	10	7	14.3	22.6
Uranium-235	WSCF	10	4	25.0	82.0
Uranium-238	WSCF	10	8	37.5	23.4 - 35.1

^{*} Meets the evaluation criterion that the sample-duplicate pair has at least one result greater than or equal to five times the method detection limit or the minimum detectable activity.

RPD = relative percent difference

GEL = GEL Laboratory

TARL = TestAmerica Richland

TASL = TestAmerica St. Louis

WSCF = Waste Sampling and Characterization Facility

By laboratory, TestAmerica Richland had the lowest laboratory sample duplicate success: of its 116 sample duplicates that met the evaluation criterion, 109 met the 20% limit for a 94.0% success rate. The seven sample duplicate failures were for coliform bacteria and iodine-129. For coliform bacteria, only three sample duplicates met the evaluation criterion, and all three duplicates failed with RPDs that ranged from 31.3% to 102.4%. For iodine-129, TARL had a 21.1% failure rate for four sample duplicates with RPDs that ranged from 26.7% to 54.4%.

GEL reported 75 laboratory sample duplicate results that met the evaluation criterion with 72 (96.0%) that met RPD criteria. The three RPD failures were one each for total organic halides, cyanide, and iodine-129.

TASL reported 166 laboratory sample duplicate results that met the evaluation criterion with 163 (98.2%) that met the 20% RPD criterion. The three RPD failures were one each for total organic carbon, cyanide, and sulfide.

WSCF reported 1,136 sample duplicate results that met the evaluation criterion with 1,117 (98.3%) that met the 20% RPD criterion. The 19 sample duplicate failures were for the radiochemical parameters: gross alpha (three), gross beta (10), plutonium-239/240 (one), uranium-233/234 (one), uranium-235 (one), and uranium-238 (three). The gross alpha RPDs ranged from 22.4% to 60.2%, and the gross beta RPDs ranged from 22.2% to 112.6%.

The 222-S Laboratory and Eberline Services also reported a few laboratory sample duplicates that met the evaluation criterion; none of these duplicates failed the RPD criteria.

By analyte class, the radiochemical parameters had the most laboratory sample duplicate failures: of the 315 duplicates that met the evaluation criterion, 24 (8.4%) failed the RPD criteria. These failures are discussed in the previous paragraphs. For the general chemical parameters, 133 duplicates met the evaluation criterion with five (3.8%) failures: coliform bacteria (three), total organic halides (one), and total organic carbon (one).

F.9.5 Surrogates and Surrogate Duplicates

Surrogates and surrogate duplicates are used to monitor percent recovery and precision during the analysis of samples for total petroleum hydrocarbons (TPHs), VOCs, and SVOCs. Surrogates are typically deuterated, fluorinated, or brominated organic compounds with chemical properties similar to those of the analytes of interest in a sample but are not normally found in groundwater samples. Known amounts of the surrogates are added to the sample prior to sample preparation and analysis to monitor the recovery of the organic compounds during the analytical process.

For the current reporting period, GEL, TASL, and WSCF reported surrogate data for TPHs, VOCs, and SVOCs. As Table F.1 indicates, percent recoveries for surrogates are compared to statistically derived laboratory-specific process control limits. The precision limit for surrogate duplicate RPDs was 20% unless the laboratory provided a statistically derived precision limit. The laboratories may apply a laboratory qualifier of X and an accompanying explanatory note in the data report or case narrative when laboratory surrogate/surrogate duplicate percent recoveries or RPDs are outside QC limits. GEL reported only 275 surrogate results and eight surrogate duplicate results with no failures and will not be discussed further in this section.

Tables F-15 and F-16 indicate that 98.8% of the percent recoveries for the 7,701 reported surrogates and 95.1% of the RPDs for the 635 reported surrogate duplicates met the QC criteria for CY2013. These success rates, along with those for the other measures of laboratory accuracy and precision, continue to provide assurance that the laboratories are producing data with sufficient accuracy and precision to meet the needs of the groundwater monitoring program. The CY2013 surrogate success rates are similar to the CY2012 success rates of 98.4% for surrogate percent recoveries and 98.1% for surrogate RPDs and the CY2011 success rates of 97.5% for surrogate percent recoveries and 98.0% for surrogate RPDs. Table F.21 lists the out-of-limit surrogate results for the current reporting period.

Table F.21. Surrogate Out-of-Limit Results

				Percent	Percent	Number of	Percent
Surrogate	Lab	Method	Number of Surrogates	Out of Limit Low	Out of Limit High	Surrogate Duplicates	RPD Out of Limit*
· ·	cal Param	eters: Recovery Lii		ratory Spec	ific (Statisti	cally Derive	d)
o-Terphenyl	WSCF	WTPH_DIESEL	168	1.8	_	25	8.0
Volatile Organi	ic Compo	unds: Recovery Lin	nits = Labor	atory Speci	fic (Statistic	ally Derive	d)
1,2-Dichloroethane-d4	TASL	8260_VOA_GCMS	175	_	2.9	_	_
1,2-Dichloroethane-d4	WSCF	8260_VOA_GCMS	1,096	0.4	0.5	93	1.1
4-Fluorobromobenzene	TASL	8260_VOA_GCMS	175	_	3.4	_	_
4-Fluorobromobenzene	WSCF	8260_VOA_GCMS	1,096	_	0.7	93	_
Dibromofluoromethane	TASL	8260_VOA_GCMS	175	_	2.9	_	_
Toluene-d8	TASL	8260_VOA_GCMS	175	_	1.1	_	_
Toluene-d8	WSCF	8260_VOA_GCMS	1,096	_	1.1	93	1.1
Semivolatile Orga	anic Comp	oounds: Recovery l	Limits = Lab	oratory Spe	ecific (Statis	stically Deri	ved)
2,2',3,3',4,4',5,5',6,6'- Decachlorobiphenyl	TASL	8081_PEST_GC	80	1.3	_	_	_
2,4,5,6-Tetrachloro-m- xylene	TASL	8081_PEST_GC	79	1.3	3.8	_	_
2,4,5,6-Tetrachloro-m- xylene	WSCF	8082_PCB_GC	38	7.9		8	12.5

Table F.21. Surrogate Out-of-Limit Results

Surrogate	Lab	Method	Number of Surrogates	Percent Out of Limit Low	Percent Out of Limit High	Number of Surrogate Duplicates	Percent RPD Out of Limit*
2,4,6-Tribromophenol	TASL	8270_SVOA_GCMS	10	_	10.0	_	_
2,4,6-Tribromophenol	WSCF	8270_SVOA_GCMS	420	1.2	_	47	10.6
2-Fluorobiphenyl	WSCF	8270_SVOA_GCMS	290	_	_	31	6.5
2-Fluorophenol	WSCF	8270_SVOA_GCMS	290	2.4	_	31	12.9
2-Methylnaphthalene- d10	WSCF	8270_SVOA_GCMS	290	_	_	31	6.5
Fluoranthene-d10	WSCF	8270_SVOA_GCMS	290	2.1	_	31	6.5
Nitrobenzene-d5	WSCF	8270_SVOA_GCMS	290	_	_	31	6.5
Phenol-d5	WSCF	8270_SVOA_GCMS	290	2.8	_	31	19.4
p-terphenyl-d14	TASL	8270_SVOA_GCMS	60	6.7	_	_	_
Terphenyl-d14	WSCF	8270_SVOA_GCMS	419	_	_	47	6.4

^{*} Sample duplicate RPD limit of 20% was used to evaluate surrogate duplicates.

RPD = relative percent difference

TASL = TestAmerica St. Louis Laboratory

WSCF = Waste Sampling and Characterization Facility

By laboratory, TASL had the lowest surrogate percent recovery rate at 97.7%; TASL reported no surrogate duplicate results. The largest surrogate recovery failure was for VOCs with a 2.5% failure rate; all 18 surrogate recoveries exceeded the upper recovery limit. The TASL VOC surrogate recovery failures were traced to two analytical batches with very similar recovery values for the surrogate spikes. This may indicate that the high recoveries were due to a systematic spiking error rather than errors associated with sample treatment and analysis. For the SVOCs, the surrogate recovery failure rate was 1.2% low and 0.8% high. Of the 31 surrogate percent recoveries TASL reported for TPH – gasoline, none were outside the QC limits.

WSCF had the next lowest surrogate recovery percent recovery rate at 99.0% and the lowest RPD acceptance rate at 95.1%. For the TPH analyses, WSCF reported three (1.3%) of the surrogates outside of control limits, all failing low, and two (4.3%) surrogate RPDs that exceeded the 20% limit. Surrogate recovery failures for WSCF's VOC analysis was 0.9%, with four failing low and 25 failing high. Seventeen of the high surrogate recoveries were traced to a single batch and had similar recovery values. This may indicate that these high recoveries were due to a systematic spiking error rather than errors associated with sample treatment and analysis. Two (0.7%) VOC surrogate RPDs exceeded the 20% limit. For the SVOCs, WSCF reported 29 (1.1%) of the surrogate recoveries outside control limits; all fell below the lower control limit. The RPD failure rate for WSCF's surrogate duplicates was 9.1% for the SVOCs. Seventeen of the 27 SVOC surrogate duplicate failures were traced to three samples in three separate batches; the percent recoveries for the surrogate compounds within each sample were very similar and again may indicate a systematic error with the surrogate spike addition to those samples rather than an analyte recovery issue during sample extraction and analysis.

By analyte class, general chemical parameters (TPH), VOCs and SVOCs had similar surrogate recovery success rates of about 98.8%. For the 264 TPH surrogate results, three failed low and none high, and for the 47 associated surrogate duplicates, two had RPDs greater than the 20% RPD limit. Of the 4,284 VOC surrogate results, four failed low and 43 failed high; these high recoveries are discussed in the previous

two paragraphs. Of the 3,153 SVOC surrogate results reported, 35 had recoveries less than the lower recovery limit, and four exceeded the upper recovery limit for a total failure rate of 1.2%. Many of the low recovery failures may be due to systematic surrogate spiking errors as discussed in the previous paragraph.

F.10 Laboratory Performance

During CY2013, laboratory performance was tracked using two methods: the groundwater quarterly blind standards program and laboratory performance evaluation programs. The results of the blind standards program are discussed in Section F.10.1 and the laboratory performance evaluation programs are discussed in Section F.10.2.

F.10.1 Quarterly Blind Standard Evaluations

The groundwater monitoring program issues blind standards to the supporting laboratories to provide a measure of intra- and inter-laboratory precision and accuracy. These standards help groundwater staff troubleshoot analytical problems identified through data reviews and QC evaluations. The blind standards also may be used to confirm the adequacy of corrective actions to resolve analytical problems. Blind standards are required to be submitted to the participating laboratories on a quarterly basis (DOE/RL-91-50 and CHPRC-00189); this requirement was met during CY2013. The quality requirements and control limits for the groundwater monitoring blind standards are given in DOE/RL-91-50 and CHPRC-00189 and are listed in Table F.22. A *success rate* is calculated for the results returned by each supporting laboratory:

Success Rate =
$$\frac{\text{number of results meeting QC recovery criteria}}{\text{total number of results reported}} \times 100$$
 (Equation F-4)

The acceptance criterion for the success rate is 80% (CHPRC-00189).

Table F.22. Groundwater Blind Standard Recovery and Precision Requirements^{a,b}

Analyte Class	Recovery Limits (% Recovery)	Precision Limit ^c (% RSD)
General Chemical Parameters	75 - 125	≤ 25
Ammonia and Anions	75 - 125	≤ 25
Metals	80 - 120	≤ 20
Volatile Organic Compounds	75 - 125	≤ 25
Semivolatile Organic Compounds ^d	n/r	n/r
Radiological Parameters	70 - 130	≤ 20

a. Sources: DOE/RL-91-50, Hanford Site Environmental Monitoring Plan, and CHPRC-00189, CH2M HILL Plateau Remediation Company Environmental Quality Assurance Program Plan.

n/r = not required

RSD = relative standard deviation

b. Blind standards are required to be submitted to participating laboratories on a quarterly basis; the identity of the analytes and their concentrations vary from quarter to quarter.

c. If the results are less than five times the required detection limit, then the criterion is that the difference of the results of the replicates is less than the required detection limit.

d. The blind standards program does not require semivolatile organic compound standards.

During CY2013, the groundwater monitoring program sent blind standards to GEL, TARL, TASL, and WSCF. In summary, the evaluation of the double-blind standards for 2013 indicates that, with some exceptions, the participating laboratories generally met the 80% success rate requirement for the groundwater monitoring program. Performance was somewhat uneven over the reporting period with TARL and TASL turning in one quarter with a success rate less than 80%. Of the blind results for all laboratories for 2013, 85.8% of the blind sample determinations were acceptable. This percentage is similar to the historical success rates of 88.5% for 2012, 83.6% for 2011, and 86.6% for 2010. Table F.23 presents the success rates for each laboratory by quarter during CY2013.

Table F.23.	Blind Standards Laborato	ory Success Rates for CY2013
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	Success Rate (%) by Quarter ^a					
Laboratory	Q1	Q2	Q3	Q4		
GEL ^b	n/a	n/a	86.9	86.7		
TARL	86.7	80.6	87.9	76.7		
TASL	87.9	93.0	76.7	85.4		
WSCF	91.1	86.7	86.1	83.2		

a. Success Rate = 100 x number of results within QC recovery criteria / total number of results submitted. The minimum acceptable success rate is 80% (CHPRC-00189, *CH2M HILL Plateau Remediation Company Environmental Quality Assurance Program Plan*). Success rates less than the 80% criterion are denoted by shaded cells.

n/a = not applicable

GEL = GEL Laboratory

TARL = TestAmerica Richland Laboratory

TASL = TestAmerica St. Louis Laboratory

WSCF = Waste Sampling and Characterization Facility

Blind standards were generally prepared in triplicate and submitted to the laboratories to check the accuracy and precision of analyses. For most constituents, the blind standards were prepared in a groundwater matrix from an appropriate background well to simulate actual groundwater samples. Standards for specific conductance were commercially prepared in deionized water; starting the third quarter, the conductivity standard was dropped because conductivity is rarely requested as a laboratory analyte. Multi-metal blind standards for analysis by ICP techniques were prepared in deionized water using commercially prepared metals standards. The blind standards were submitted to the laboratories as regular groundwater samples.

After analysis, the laboratories' results were compared with the spiked concentrations to generate percent recoveries and the %RSDs were determined for the results. The percent recoveries and %RSDs were compared to the control limits to determine whether the data met the QC criteria³. Out-of-limit results were reviewed for errors. In situations where several results for the same method were unacceptable, an RDR may be generated to reanalyze the blind samples (if within holding times) or for recheck of the

b. GEL's first participation in the quarterly blinds program was the third quarter of this reporting period.

³ If the blind standard concentration is less than five times the required detection limit for the analyte, the secondary precision criterion is used: the difference between the maximum and minimum value reported must be less than the required detection limit (DOE/RL-91-50).

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results. Any remaining out-of-limit results were discussed with the laboratory, potential problems were investigated, and corrective actions were requested when appropriate. Table F.24 summarizes the blind standards that exceeded the recovery or precision criteria during 2013; results that are outside the recovery or precision limits are in shaded cells.

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Table F.24. CY2013 Blind Standard Out-of-Limit Results

			i abie i	.24.	CIZUI	Dilliu St	anuaru Ot	it-ot-Limit	resuits				
Constituent	Lab	Spike Value	RDL	MDL / MDA	Units	Recovery Limits (%)	Recovery 1 (%)	Recovery 2 (%)	Recovery 3 (%)	Recovery 4 (%)	Precision Limit (%)	Precision (%RSD)	Precision Criterion Exceeded?
	First Quarter Results												
TOC	TASL	1,000	1,000	270	μg/L	75 - 125	120.0	130.0	130.0	160.0	25	12.8	N*
TOX (VOA)	TASL	498	10	1.8	μg/L	75 - 125	76.1	79.9	74.5	_	25	3.6	N
TOX (VOA)	WSCF	498	10	25	μg/L	75 - 125	60.6	71.9	77.1		25	12.0	N
Antimony	TASL	5	60	4	μg/L	80 - 120	138.0	160.0	144.0	_	20	7.7	N*
Boron	TASL	25	20	10	μg/L	80 - 120	286.0	352.8	238.8	_	20	19.6	Y*
Silver	WSCF	5	10	4	μg/L	80 - 120	146.4	151.6	144.4	_	20	2.6	N*
Uranium	WSCF	148	15	0.1	μg/L	80 - 120	120.6	122.6	120.6	_	20	1.0	N
Uranium	WSCF	148	25	0.1	μg/L	80 - 120	121.3	130.8	119.9	_	20	4.8	N
Vanadium	TASL	5	10	4.1	μg/L	80 - 120	84.0	142.0	156.0	_	20	30.0	N*
Zinc	TASL	25	5	5.2	μg/L	80 - 120	121.6	124.0	130.8	_	20	3.8	N
Carbon-14	TASL	205.9	3	8.34	pCi/L	70 - 130	67.5	59.3	81.1		20	15.9	N
Gross alpha	TARL	305.8	3	3.19	pCi/L	70 - 130	63.5	63.5	62.5	_	20	0.9	N
Gross alpha	WSCF	305.8	4	3.2	pCi/L	70 - 130	72.0	85.0	68.7	_	20	11.5	N
Gross beta	WSCF	26.14	1	13	pCi/L	70 - 130	176.0	160.7	160.7	_	20	5.3	N
Plutonium-239	TARL	1.59	1	0.199	pCi/L	70 - 130	94.3	61.1	126.4	_	20	34.9	Y*
	-				Sec	ond Quart	er Results						
TOC	TASL	1,500	1000	270	μg/L	75 - 125	126.7	140.0	140.0	133.3	25	4.7	N*
TOX (VOA)	WSCF	273	10	25	μg/L	75 - 125	59.3	59.7	67.4	68.9	25	7.8	N
Nitrite	WSCF	2,176	75	125	μg/L	75 - 125	64.3	62.0	63.0	_	25	1.8	N
Boron	TASL	49.4	20	10	μg/L	80 - 120	121.3	100.8	118.2	_	20	9.7	N*
Boron	WSCF	49.4	20	1	μg/L	80 - 120	111.3	143.7	123.5	_	20	13.0	N*
Mercury	TASL	5.00	0.5	0.3	μg/L	80 - 120	122.0	118.0	120.0	_	20	1.7	N
Uranium	TARL	298	1	0.08	μg/L	80 - 120	112.1	120.5	110.1	_	20	4.8	N
Uranium	WSCF	296	1	0.10	μg/L	80 - 120	114.9	120.3	118.9	_	20	2.4	N
Carbon tetrachloride	WSCF	495	5	10	μg/L	75 - 125	129.3	125.3	123.2		25	2.5	N
Chloroform	WSCF	201	5	10	μg/L	75 - 125	129.4	119.4	119.4	_	25	4.7	N

Table F.24. CY2013 Blind Standard Out-of-Limit Results

_			i abie i	.24.	CIZUIS	Dilliu St	anuaru Ou	it-or-Limit	Results				
Constituent	Lab	Spike Value	RDL	MDL / MDA	Units	Recovery Limits (%)	Recovery 1 (%)	Recovery 2 (%)	Recovery 3 (%)	Recovery 4 (%)	Precision Limit (%)	Precision (%RSD)	Precision Criterion Exceeded?
Gross alpha	TARL	50.0	3	1.59	pCi/L	70 - 130	68.4	63.2	74.6	_	20	8.3	N
Gross alpha	WSCF	50.0	3	3.9	pCi/L	70 - 130	52.0	83.9	64.0	_	20	24.2	Y
Strontium-90	TARL	9.81	2	1.76	pCi/L	70 - 130	123.3	109.1	141.7	_	20	13.1	Y*
Technetium-99	TARL	208	15	9.08	pCi/L	70 - 130	52.9	32.7	45.4	_	20	23.5	Y
	-		-	-	Th	ird Quarte	r Results	-	-	-	-	-	-
TOC	TASL	2,237	1000	270	μg/L	75 - 125	125.2	138.6	138.6	147.5	25	6.7	N*
TOX (VOA)	GEL	44	10	3.33	μg/L	75 - 125	79.0	73.3	58.4	_	25	15.1	N*
TOX (VOA)	WSCF	44	10	25	μg/L	75 - 125	63.9	129.5	110.0	_	25	33.3	Y*
Cyanide	GEL	300	5	8.35	μg/L	75 - 125	130.0	134.7	92.3	_	25	19.5	N
Nitrite	GEL	251	250	125	μg/L	75 - 125	58.1	60.1	58.9	_	25	1.7	N*
Nitrite	TASL	251	250	9.85	μg/L	75 - 125	40.6	40.6	39.2	_	25	2.0	N*
Nitrite	WSCF	251	250	131	μg/L	75 - 125	52.1	52.1	52.1	_	25	0.0	N*
Copper	WSCF	25	10	4.00	μg/L	80 - 120	82.6	76.3	78.3	_	20	4.1	N*
Nickel	TASL	25	40	13.3	μg/L	80 - 120	131.2	129.6	132.0	_	20	0.9	N*
Uranium	GEL	101	1	0.335	μg/L	80 - 120	117.4	120.4	116.4	_	20	1.8	N
Uranium	TASL	101	20	23.5	μg/L	80 - 120	23.4	58.5	56.7	_	20	42.8	Y
Uranium	TASL	101	1	0.23	μg/L	80 - 120	111.4	104.5	120.4	_	20	7.1	N
Uranium	WSCF	101	11	0.1	μg/L	80 - 120	150.2	119.4	111.4	_	20	16.1	N
Carbon tetrachloride	GEL	244	5	1.5	μg/L	75 - 125	141.0	129.9	131.6		25	4.5	N
Chloroform	TASL	50	5	0.10	μg/L	75 - 125	78.0	70.0	74.0		25	5.4	N
Tetrachloroethene	TASL	20	5	0.18	μg/L	75 - 125	84.2	69.3	74.3	_	25	10.0	N*
Tetrachloroethene	WSCF	20	5	1	μg/L	75 - 125	74.3	69.3	64.4		25	7.1	N*
Trichloroethene	TASL	49.3	5	0.25	μg/L	75 - 125	79.1	66.9	73.0	_	25	8.3	N
Gross alpha	TARL	100	3	3.7	pCi/L	70 - 130	72.3	62.8	60.8		20	9.5	N
Gross alpha	WSCF	100	3	3.7	pCi/L	70 - 130	71.9	65.9	69.9	_	20	4.4	N
Gross beta	TARL	109	4	3.79	pCi/L	70 - 130	55.5	84.7	98.9	_	20	27.8	Y
Iodine-129	GEL	5.1	1	1.14	pCi/L	70 - 130	123.3	138.7	113.2	_	20	10.3	N

Table F.24. CY2013 Blind Standard Out-of-Limit Results

			i abie i	.24.	CIZUIS	Dilliu St	anuaru Ou	it-or-Limit	Nesuits				
Constituent	Lab	Spike Value	RDL	MDL / MDA	Units	Recovery Limits (%)	Recovery 1 (%)	Recovery 2 (%)	Recovery 3 (%)	Recovery 4 (%)	Precision Limit (%)	Precision (%RSD)	Precision Criterion Exceeded?
Plutonium-239	GEL	2.1	1	0.81	pCi/L	70 - 130	65.9	75.6	38.4	_	20	32.5	N*
Plutonium-239	TARL	2.1	1	0.24	pCi/L	70 - 130	86.3	76.1	56.1	_	20	21.5	N*
Plutonium-239	WSCF	2.1	1	0.067	pCi/L	70 - 130	68.3	73.2	78.0	_	20	6.7	N*
					Fou	ırth Quarte	er Results						
TOC	GEL	499	1000	330	μg/L	75 - 125	111.8	112.0	67.5	106.4	25	21.6	N*
TOC	WSCF	499	1000	100	μg/L	75 - 125	214.4	214.4	216.4	216.4	25	0.5	N*
TOX (phenol)	WSCF	100	10	25	μg/L	75 - 125	121.5	138.6	50.6	116.5	25	36.2	Y
TOX (VOA)	GEL	98.2	10	3.33	μg/L	75 - 125	72.0	79.2	79.8	_	25	5.7	N
TOX (VOA)	TASL	98.2	10	1.8	μg/L	75 - 125	77.9	74.8	72.9	_	25	3.3	N
Nitrite	WSCF	1,040	250	131	μg/L	75 - 125	72.0	71.7	82.8		25	8.3	N*
Antimony	TASL	5	5	1.7	μg/L	80 - 120	210.0	188.0	240.0	_	20	12.3	N*
Arsenic	TASL	5	2	1.20	μg/L	80 - 120	112.0	102.0	128.0	_	20	11.5	N*
Boron	TASL	50	20	10	μg/L	80 - 120	136.6	149.5	214.1	_	20	24.9	Y*
Hexavalent chromium	TARL	25	10	8	μg/L	80 - 120	217.4	213.4	213.4	_	20	1.1	N*
Hexavalent chromium	WSCF	25.3	10	2	μg/L	80 - 120	222.5	218.6	227.3	_	20	2.0	N*
Lead	GEL	5.0	2	0.5	μg/L	80 - 120	110.0	121.4	124.2	_	20	6.3	N*
Uranium	GEL	19.5	1	0.067	μg/L	80 - 120	127.2	133.8	133.8	_	20	2.9	N
Uranium	TARL	22	1	0.0835	μg/L	80 - 120	79.0	74.3	78.5	_	20	3.3	N
Vanadium	GEL	5	10	1	μg/L	80 - 120	119.8	121.6	116.4	_	20	2.2	N*
Vanadium	WSCF	5	10	0.4	μg/L	80 - 120	102.6	121.2	116.4	_	20	8.5	N*
Carbon tetrachloride	GEL	5	1	0.3	μg/L	75 - 125	93.0	64.6	78.4	_	25	18.1	N
Carbon tetrachloride	TASL	5	1	0.13	μg/L	75 - 125	52.0	92.0	94.0	_	25	29.9	Y
Tetrachloroethene	GEL	98	5	0.3	μg/L	75 - 125	83.3	62.0	72.3	_	25	14.7	N
Tetrachloroethene	TASL	98	5	0.9	μg/L	75 - 125	63.5	86.0	85.0	_	25	16.3	N
Tetrachloroethene	WSCF	98	5	1	μg/L	75 - 125	88.0	70.6	93.1	_	25	14.1	N
Trichloroethene	GEL	5	1	0.3	μg/L	75 - 125	92.9	68.3	78.8	_	25	15.4	N
Trichloroethene	TASL	5	1	0.25	μg/L	75 - 125	65.4	78.8	80.8	_	25	11.2	N

Table F.24. CY2013 Blind Standard Out-of-Limit Results

Constituent	Lab	Spike Value	RDL	MDL / MDA	Units	Recovery Limits (%)	Recovery 1 (%)	Recovery 2 (%)	Recovery 3 (%)	Recovery 4 (%)	Precision Limit (%)		Precision Criterion Exceeded?
Trichloroethene	WSCF	5	1	0.5	μg/L	75 - 125	78.8	61.5	73.1	_	25	12.4	N
Carbon-14	TASL	498	5	15.9	pCi/L	70 - 130	63.1	95.0	90.4		20	20.8	Y
Gross alpha	TARL	23	3	2.74	pCi/L	70 - 130	69.9	74.7	71.6	_	20	3.3	N
Gross alpha	WSCF	23	3	3	pCi/L	70 - 130	90.6	18.6	60.4	_	20	64.0	Y
Gross beta	WSCF	37	4	6.2	pCi/L	70 - 130	121.4	37.8	118.7	_	20	51.3	Y
Iodine-129	GEL	3	1	1.6	pCi/L	70 - 130	135.5	163.8	70.8	_	20	38.7	Y*
Plutonium-239	GEL	20	1	0.58	pCi/L	70 - 130	98.5	95.0	64.8	_	20	21.5	Y

^{*} The blind standard concentration was less than five times the required detection limit for this analyte. Hence, the secondary precision criterion was used: the difference between the maximum and minimum value reported must be less than the required detection limit.

MDA = minimum detectable activity

MDL = method detection limit

RDL = required detection limit

RSD = relative standard deviation

GEL = GEL laboratory

TARL = TestAmerica Richland Laboratory

TASL = TestAmerica St. Louis laboratory

WSCF = Waste Sampling and Characterization Facility

The most notable observations for the CY2013 blind standards were:

- Total organic carbon: During the first three quarters of the reporting period, TASL returned TOC recoveries that exceeded the upper recovery limit with a range of 126% to 160%; the acceptable recovery range is 75% to 125%. Between the third and fourth quarters of the calendar year, a request was submitted to TASL to check their TOC method. In response, TASL modified its TOC method to more completely purge inorganic carbon from groundwater samples prior to determination of TOC. For the last quarter of CY2013, the TASL TOC recoveries ranged from 76.2% to 94.2%. For that same last quarter WSCF reported TOC percent recoveries that ranged from 214% to 216%. During the previous three quarters, WSCF reported TOC recoveries that were greater than 100%, but less than the upper recovery limit of 125%. Based on these observations, some of the TASL and WSCF TOC data reported during CY2013 may have a possible high bias, especially the TASL TOC data reported during the first three quarters of the year.
- Total organic halides: Two types of standards were used to generate TOX blind samples each quarter: one based on the relatively non-volatile compound 2,4,5-trichlorophenol and one based on the same standards as those used for the VOC blind standard containing carbon tetrachloride, chloroform, tetrachloroethene, and trichloroethene. For the trichlorophenol-based standard, most of the recoveries reported by GEL, TASL, and WSCF were within the 75% and 125% recovery limits. In contrast, the VOA-based TOX standards showed generally low recoveries with all three laboratories reporting some TOX recoveries less than the lower recovery limit of 75%. Out-of-limit low recoveries ranged from 58.4% to 74.8%. WSCF reported one out-of-limit high recovery at 129% for the VOA-based TOX standards. The predominantly low recoveries may reflect TOX recoveries for actual groundwater samples because the TOX content of many Hanford-Site groundwater samples is likely due to volatile organic compounds.
- *Nitrite*: With a few exceptions, GEL and TASL reported nitrite recoveries within the recovery limits of 75% to 125% when the nitrite concentration was well above the laboratory's MDL. WSCF reported nitrite recoveries less than the lower recovery limit for the last three quarters of CY2013 However, all three laboratories under-reported nitrite when the nitrite concentration was near the laboratory's MDL (see the third quarter nitrite recoveries in Table F.24); a similar observation was noted for the CY2012 nitrite results. This implies that nitrite may be under-reported in Hanford Site groundwater samples with possible false negatives for nitrite in these types of samples.
- Metals: All four participating laboratories returned results for metals blind standards during CY2013. GEL, TASL, and WSCF reported metals determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) and inductively coupled plasma mass spectrometry (ICP-MS). TARL and WSCF reported hexavalent chromium by colorimetry, and GEL and TARL reported total uranium by kinetic phosphorescence analysis (KPA). The recovery acceptance limits for the metals are 80% to 120%. With a few exceptions, the ICP metals with out-of-limit recoveries exceeded the upper 120% limit. These metals included antimony, arsenic, boron, lead, mercury, nickel, silver, uranium, vanadium, and zinc, and their associated out-of-limit recoveries ranged from 121% to 353%. The following bullets present notable results for the CY2013 metal blind standards.
 - Boron by ICP-MS: Boron results were reported for the first, second, and fourth quarters of CY2013. For seven of the nine blind standards analyzed for boron, TASL reported results that exceeded the 120% upper limit with recoveries ranging from 121% to 353%. This continues a trend observed in CY2011 and CY2012. TASL has indicated that it will switch from ICP-MS (EPA method 6020) to ICP-AES (EPA method 6010) to report future boron results. WSCF also

- reported high boron recoveries by ICP-MS for the second quarter blind standards, but no trend for high or low recoveries for WSCF boron results has been established.
- Hexavalent chromium: Hexavalent chromium blind standards were sent to the TARL and WSCF laboratories all four quarters of CY2013. Both laboratories returned results within the 80% to 120% recovery limits except for the third quarter. The third quarter recoveries for the two laboratories were nearly identical and ranged from 213% to 217% for TARL and from 219% to 227% for WSCF. These results imply a possible error in making the hexavalent chromium standard for that quarter, but such an error could not be confirmed. In any event, most of the hexavalent chromium blind standards data indicate that the reporting laboratories are generating accurate results for that analyte.
- Uranium: Uranium blind standards were submitted all four quarters of CY2013 to all four laboratories. To generate their uranium results, GEL used ICP-MS and KPA, TARL used KPA, TASL used ICP-AES and ICP-MS, and WSCF used ICP-MS. With two exceptions, the laboratories reported blind-standard uranium results that trended high during the reporting period. GEL reported results within limits, although trending high, except for their fourth quarter ICP-MS recoveries that ranged from 127% to 134%. TARL also reported results within limits except for their fourth quarter recoveries that ranged from 74.3% to 79.0%. TASL reported results within limits, again mostly trending high, with the exception of their third quarter ICP-AES recoveries that ranged from 23.4% to 58.5%. The third quarter was the only quarter TASL reported uranium blind results by ICP-AES, so these recoveries do not represent the blind recoveries TASL generally reports for their ICP-MS method. For CY2013, WSCF reported uranium blind recoveries that uniformly trended high with seven recoveries that exceeded the 120% recovery limit ranging from 121% to 150%. A corrective action is in place to evaluate the high recoveries frequently observed for the uranium blind standards. A new mass-based (as opposed to isotopicbased) uranium standard has been obtained for blind standards make-up during CY2014 to help elucidate the source of the apparent high bias in the uranium blind standard results.
- Volatile Organic Compounds: TASL and WSCF reported results for VOC blind standards during CY2013; GEL reported results for the third and fourth quarters only. The recovery acceptance limits for the VOCs are 75% to 125%. The VOC blind standards contained carbon tetrachloride, chloroform, tetrachloroethene, and trichloroethene at concentrations that ranged from 5 to 500 μg/L. All the first quarter VOC results from TASL and WSCF were within the acceptance criteria. For the second quarter, WSCF reported recoveries for carbon tetrachloride and chloroform that trended high with three results that exceeded the upper recovery limit of 125%. For the third quarter, GEL also reported recoveries for carbon tetrachloride that exceeded the upper recovery limit. Otherwise, most of the third and fourth quarter recoveries trended low with a number of recoveries less than the lower recovery limit of 75%; this continues the historical trend of low recoveries for the VOC blind standards. Low recoveries for these analytes are attributed in part to losses of the VOCs from those blind standards during standards make-up and sample handling.
- Radiochemical parameters: All four participating laboratories returned results for radiochemical blind standards during CY2013; GEL returned results for the third and fourth quarters only. The recovery acceptance limits for radiochemical parameters are 70% to 130%. The following bullets discuss the highlights of those results.
 - Carbon-14: For the second quarter of CY2011 and the first quarter of CY2012, TARL had
 reported recoveries for carbon-14 less than the lower recovery limit of 70%. Those low recoveries
 were traced to TARL's sample preparation method which was subsequently modified to remedy

the low recoveries. Starting the fourth quarter of CY2012 and continuing through CY2013, TARL returned carbon-14 recoveries well within the 70% to 130% recovery limits. TASL reported some carbon-14 recoveries less than the lower recovery limit for the first and fourth quarters of CY2013, but the carbon-14 recoveries for the second and third quarters were well within the recovery limits.

- Gross alpha: GEL, TARL, and WSCF returned gross alpha results for this reporting period. TARL and WSCF reported 12 gross alpha results each during CY2013; the recoveries for these results all trended less than 100% with a total of 15 recoveries less than the lower recovery limit of 70% for this analysis. A corrective action is in place to investigate and resolve the low recovery issue at the two laboratories. For the two quarters that GEL analyzed gross alpha blind standards, the laboratory reported recoveries well within the 70% to 130% recovery limits.
- Iodine-129: GEL and TARL reported 18 results for iodine-129 blind standards during CY2013. The recoveries for 16 results were greater than 100%, and three GEL recoveries exceeded the 130% upper acceptance limit. TARL did not report any iodine-129 recoveries outside the acceptance limits. This tendency of the recoveries to trend high may indicate a slight high bias in the determination of iodine-129 in Hanford Site groundwater samples.
- Plutonium-239: GEL, TARL, and WSCF returned plutonium-239 blind standard results for CY2013. TARL reported recoveries largely within the 70% and 130% recovery limits. Most of these recoveries were less than 100%, and two recoveries, one in the first quarter and one in the third quarter, were less than the 70% lower acceptance limit. The first quarter results for TARL exceeded the 20% precision criterion as well. WSCF likewise reported recoveries within the recovery limits; most of the recoveries were less than 100%, and one recovery for the third quarter was less than the lower acceptance limit. For the two quarters that GEL reported plutonium-239 blind standard results, the laboratory reported recoveries less than 100% with three recoveries less than the lower acceptance limit. For the fourth quarter, the precision of the GEL plutonium-239 results exceeded the %RSD precision limit of 20%. The tendency of all three laboratories to report plutonium-239 recoveries less than 100% may indicate a slight low bias in the determination of plutonium-239 in Hanford Site groundwater samples.

F.10.2 Laboratory Performance Evaluation Studies

Laboratories that generate groundwater monitoring data are required to participate in nationally recognized performance evaluation studies on at least an annual basis (CHPRC-00189); this requirement was met for CY2013. During CY2013, Environmental Resources Associates (ERA) and DOE conducted national studies to evaluate laboratory performance for chemical and radiological constituents. GEL, TARL, TASL, and WSCF participated in the EPA-sanctioned water pollution/supply (WP/WS) performance evaluation studies conducted by ERA. GEL, TARL, TASL, and WSCF also participated in ERA's InterLaB RadCheM Proficiency Testing Program (RAD) and in DOE's Mixed Analyte Performance Evaluation Program (MAPEP). The results of those studies related to groundwater monitoring at the Hanford Site are described in this section. Because 222-S and Eberline generated 0.1% or less of the groundwater monitoring results for CY2013, performance evaluation studies for those labs are not included here.

Water Pollution/Supply Performance Evaluation Studies

The purpose of WP/WS performance evaluation studies is to evaluate the performance of laboratories in analyzing selected organic and inorganic compounds in water matrices. An accredited agency, e.g. ERA, distributes standard water samples to participating laboratories. These samples contain specific organic

and inorganic analytes at concentrations unknown to the participating laboratories. After analysis, the laboratories submit results to the accredited agency, which uses regression equations to determine acceptance and warning limits for the study participants. The results of these studies are expressed as a percentage of the results that the accredited agency found acceptable and independently verify the level of laboratory performance. If there is an unacceptable result, the laboratories may order an ERA QuiKTMResponse sample to verify successful corrective action. QuiKTMResponse samples are similar to water pollution/water supply samples, and results are reported in a comparable fashion.

For the two water pollution performance evaluation studies (ERA WP-216 and WP-222) in which WSCF participated during the reporting period, the percentage of results within the acceptance limits was 99% of 192 total results reported (Table F.25). Two constituents, Aroclor 1254 and silver, had unacceptable results; acceptable results were achieved for both of these constituents in the follow up QuiKTMResponse samples.

Table F.25. Summary of WSCF Performance Evaluation Studies

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Study Number	Date	Correct Results / Total Results						
WatR [™] Pollution/WatR [™] Supply Performance Evaluation Studies, Environmental Resource Associates								
WP-216	January 2013	85/85						
WP-222	July 2013	105/107 ^a						
DOE Mixed Analyte Performance Evaluation Program, Radiological and Environmental Sciences Laboratory								
MAPEP-13-GrW28	May 2013	2/2						
MAPEP-13-MaW28	May 2013	28/28						
MAPEP-13-OrW28	May 2013	57/57						
MAPEP-13-GrW29	November 2013	2/2						
MAPEP-13-MaW29	November 2013	30/31 ^b						
MAPEP-13-OrW29	November 2013	60/60						
InterLaB RadCheM Proficiency Testing Program, Environmental Resource Associates								
RAD-92	January 2013	4/4						
RAD-94	July 2013	8/10 °						

a. Unacceptable results were for Aroclor 1254 and silver.

For the two WP/WS performance evaluation studies in which TASL participated during 2013 (ERA WP-113, and WP-713), the percentage of results within the acceptance limits was 99% of 696 total results reported (Table F.26). As noted in Table F.26, nine different constituents had unacceptable results, none of which was repeated across studies or in more than one WP/WS study during 2013. Acceptable results were achieved in the subsequent QuiKTMResponse samples for all constituents that originally failed. As

b. Unacceptable results were for potassium-40.

c. Unacceptable results were for tritium and zinc-65.

noted, the number of constituents reported by TASL in the water pollution studies was considerably greater than those constituents reported by WSCF; therefore, the percentages from the two laboratories are not directly comparable.

For the two water pollution performance evaluation studies (ERA WP-216 and WP-222) in which TARL participated during the reporting period, the percentage of results within the acceptance limits was 98% of 47 total results reported (Table F.26). Aluminum had an unacceptable result; however, because TARL does not report this constituent for groundwater samples, the failure is not germane to groundwater monitoring data quality. Again, the number of constituents evaluated was very limited; therefore, the percentage of results is not comparable to that of the other laboratories.

Table F.26. Summary of TestAmerica Performance Evaluation Studies

		Correct Results / Total Results							
Study Number	Date	TASL	TARL						
WatR [™] Pollution/WatR [™] Supply Performance Evaluation Studies, Environmental Resource Associates									
WP-113	January 2013	340/349 ^a	_						
WP-216	January 2013		24/24						
WP-222	July 2013		22/23 ^b						
WP-713	July 201	347/347	_						
12358 Rapid Response	December 2013	21/21	_						
DOE Mixed Analyte Performance Evaluation Program, Radiological and Environmental Sciences Laboratory									
MAPEP-13-MaW28	May 2013	35/36°	19/20 ^d						
MAPEP-13-GrW28	May 2013	2/2	2/2						
MAPEP-13-XaW28	May 2013	1/1	1/1						
MAPEP-13-OrW28	May 2013	76/77 ^e	_						
MAPEP-13-MaW29	November 2013	34/35 ^f	18/19 ^g						
MAPEP-13-GrW29	November 2013	2/2	2/2						
MAPEP-13-XaW29	November 2013	1/1	1/1						
MAPEP-13-OrW29	November 2013	76/79 ^h	_						
	InterLaB RadCheM Proficiency Testing Program, Environmental Resource Associates								
RAD-93	April 2013	12/12	14/17 ⁱ						
RAD-94	July 2013	_	5/6 ^j						
RAD-95	October 2013	10/12 ^k	15/17 1						
MRAD-18	March 2013	17/17	_						

Table F.26. Summary of TestAmerica Performance Evaluation Studies

		Correct Results	/ Total Results
Study Number	Date	TASL	TARL
MRAD-19	September 2013	16/16	_

- a. Unacceptable results were for cobalt, copper, manganese, nickel, silver, 1,4-dichlorobenzene, 1,3-dichlorobenzene and benzo(a)anthracene.
- b. Unacceptable result was for aluminum.
- c. Unacceptable result was for total nickel-63.
- d. Unacceptable result was for total uranium.
- e. Unacceptable result was for 4,4'-DDT.
- f. Unacceptable result was for total nickel-63.
- g. Unacceptable result was for iron-55.
- h. Unacceptable results were for endrin, endrin ketone and heptachlor.
- i. Unacceptable results were for cesium-134, cesium-137, and total uranium.
- j. Unacceptable result was for zinc-65.
- k. Unacceptable results were for gross beta and radium-226.
- 1. Unacceptable results were for radium-226 and iodine-131.

For the twelve WP/WS performance evaluation studies in which GEL participated during 2013 (ERA WP-217, 219, 222, 223, 225, 226 and WS-198, 200, 204, and 207), the percentage of results within the acceptance limits was 94% of 784 total results reported (Table F.27). Forty-seven different constituents had unacceptable results; however 39 of these failures were due to a probable dilution error in the metals analysis and were corrected in the next run. Cyanide was missed in two separate studies however, given the large number of studies participated in by GEL with passing cyanide results the two failures do not indicate a systemic issue. All constituents with unacceptable results passed in subsequent QuiKTMResponse sample analyses.

Table F.27. Summary of GEL Performance Evaluation Studies

Study Number	Date	Correct Results / Total Results						
WatR [™] Pollution/WatR [™] Supply Performance Evaluation Studies, Environmental Resource Associates								
WP-215	February 2013	2/2						
WP-216	March 2013	1/1						
WP-217	April 2013	1/1						
WP-219	June 2013	91/92 ^a						
WP-222	September 2103	15/16 ^b						
WP-223	September 2013	62/62						
WP-225	December 2013	304/307 °						
WP-226	December 2013	4/4						
WS-198	March 2013	106/145 ^d						
WS-200	April 2013	39/39						

Table F.27. Summary of GEL Performance Evaluation Studies

Study Number	Date	Correct Results / Total Results						
WS-204	August 2013	114/116 ^e						
WS-207	November 2013	1/2 ^f						
061013C – Quick Response	June 2013	2/2						
080913 – Quick Response	August 2013	4/4						
082813 – Quick Response	August 2013	1/1						
091913E1 – Quick Response	September 2013	1/1						
091913E2 – Quick Response	October 2013	53/53						
DOE Mixed Analyte Performance Evaluation Program, Radiological and Environmental Sciences Laboratory								
MAPEP-13-GrW28	May 2013	2/2						
MAPEP-13-MaW28	May 2013	36/36						
MAPEP-13-OrW28	May 2013	76/77 ^g						
MAPEP-13-XaW28	May 2013	1/1						
MAPEP-13-GrW29	November 2013	2/2						
MAPEP-13-MaW29	November 2013	36/36						
MAPEP-13-OrW29	November 2013	79/79						
MAPEP-13-XaW29	November 2013	1/1						
	InterLaB RadCheM Proficiency Testing Program, Environmental Resource Associates							
RAD-92	January 2013	24/24						
RAD-94	July 2013	21/24 ^h						
MRAD-18	March 2013	26/26						
MRAD-19	September 2013	26/26						

- a. Unacceptable result was for copper.
- b. Unacceptable result was for iron.
- c. Unacceptable results were for ammonia, carbon tetrachloride and naphthalene.
- d. Unacceptable results were for all 6010 and 6020 metals (probable dilution factor error).
- e. Unacceptable results were for manganese and cyanide.
- f, Unacceptable result was for cyanide.
- g. Unacceptable result was for endrin aldehyde
- h. Unacceptable results were for gross alpha and strontium-89

InterLaB RadCheM Proficiency Testing Program Studies

The purpose of the RAD Proficiency Testing Program (also conducted by ERA) is to evaluate the performance of laboratories in the analysis of selected radionuclides. This program provides blind standards that contain specific amounts of one or more radionuclides in a water matrix to participating laboratories. After sample analysis, the results are forwarded to ERA for comparison with the known values and with results from other laboratories. ERA bases its control limits on the EPA's *National Standards for Water Proficiency Testing Studies, Criteria Document* (EPA NERL-Ci-0045).

During the reporting period, WSCF participated in two studies, RAD-92 and RAD-94 (Table F.25), with an acceptance percentage of 86% of 14 results with 2 unacceptable.

TARL participated in three studies, RAD-93, RAD-94, and RAD- 95 (Table F.26), with an acceptance percentage of 85% of 40 results with 6 unacceptable.

TASL participated in four studies, RAD-93, RAD-95, MRAD-18, and MRAD-19 (Table F.26), and analyzed a total of 57 constituents with an acceptance percentage of 96% with 2 unacceptable results.

GEL participated in four studies, RAD-92, RAD-94, MRAD-18, and MRAD-19, and analyzed a total of 100 constituents with an acceptance percentage of 97% with 3 unacceptable results (Table F.27).

DOE Mixed Analyte Performance Evaluation Program

DOE's MAPEP examines laboratory performance in the analysis of soil and water samples containing metals, semi-volatile organic compounds, and radionuclides. This report considers only water samples. The program is conducted at the Radiological and Environmental Sciences Laboratory in Idaho Falls, Idaho. DOE evaluates the accuracy of the MAPEP results for radiological, inorganic, and organic analytes by determining if the results fall within 30% of the reference value. Two studies were available for all labs during the reporting period: MAPEP-13-28 and MAPEP-13-29. GEL, TARL, TASL, and WSCF participated in both studies.

For the MAPEP studies, WSCF analyzed radionuclides, including inorganics, semi-volatile organics, and gross alpha/beta (Table F.25). Of 180 analytes, 179 analytes had acceptable results yielding a 99% acceptable result rate. The missed analyte was a false positive for potassium-40. This constituent had acceptable results in the previous studies.

TASL analyzed inorganics, semi-volatile organics, and radionuclides including gross alpha/beta for the MAPEP studies (Table F.26). Of 233 analytes, six had unacceptable results yielding a 97% acceptable result rate. The missed analytes were 4,4-DDT, endrin, endrin ketone, heptachlor, and nickel-63 (both studies). Except for nickel-63, all of these constituents were within limits in the preceding study, and none of the compounds are significant to Hanford groundwater monitoring.

TARL reported results for radionuclides, including gross alpha/beta, for the two MAPEP studies (Table F.26). Of 45 constituents, two had unacceptable results, yielding a 95% acceptable result rate. The missed analytes were iron-55 and total uranium. The iron-55 was also unacceptable in the preceding study but is not a constituent of concern for the Hanford groundwater.

For the two MAPEP studies, GEL analyzed inorganics, semi-volatile organics, and radionuclides, including gross alpha/beta (Table F.27). Of 234 analytes, endrin aldehyde had an unacceptable result, yielding in a 99% acceptable result rate. The missed constituent was within limits in the preceding study and the compound is not significant to Hanford groundwater monitoring.

F.11 Data Usability Conclusions

In general, this quality assessment for CY2013 groundwater monitoring data shows that the great majority of the data are useable for the purposes of groundwater monitoring. This assessment also noted some limitations in the data set. These limitations are summarized in the following subsections.

F.11.1 Data Completeness

As detailed in Section F.5 and in Tables F-2 and F-5, 99.2% of groundwater samples planned for CY2013 was collected, the requirements for the number of field QC samples were met or exceeded, and 97.4% of the analytical results met the completeness criteria. Based on the review performed in this DQA, nearly all required samples, field QC, and analytical results were collected in accordance with the groundwater monitoring requirements of DOE/RL-91-50 and CHPRC-00189.

F.11.2 Sample Preservation and Holding Time

As noted in Section F.7, improper sample preservation was a very minor issue with only 0.08% of all laboratory results affected by sample preservation issues; only 19 analyses were cancelled as a result of this issue. Missed holding times had a somewhat greater impact on the groundwater monitoring data set with 0.5% of the analytical results associated with missed holding times. Most of the results with missed holding times were still generated within two times the holding time and hence were deemed useable by the groundwater monitoring program.

F.11.3 Field Quality Control

Field QC samples were collected and analyzed in accordance with the groundwater monitoring requirements of DOE/RL-91-50 and CHPRC-00189. Field QC issues generated minimal impact to data usability. Section F.8 discusses groundwater monitoring field QC samples in detail.

For the FBs, the number and types of FBs collected met groundwater monitoring collection requirements, and 98.1% of the FB results were found to meet groundwater monitoring criteria. Of the 317 FB results that exceeded the criteria, 123 were for metals and 149 for VOCs. Many of the out-of-limit metal results were likely due to sample swaps of the FB with a groundwater sample either in the field or at the laboratory. Most of the out-of-limit VOC results were traced to probable contamination of the deionized water source used to generate the blank (methylene chloride) or to laboratory contamination during sample preparation and analysis (acetone).

For the field sample duplicates, 27.0% of the reported duplicate laboratory results met the evaluation criterion, and of these duplicate results, 94.2% were acceptable, indicating reasonable precision for field sampling operations laboratory analysis.

For the field sample TOC and TOX quadruplicates, 17.0% of the reported quadruplicate laboratory results met the evaluation criterion, and of these quadruplicate results, only 77.1% met the reproducibility criterion. This represents at best only fair reproducibility and may be linked to deficiencies in the laboratory sample preparation and analysis of these analytes. Groundwater monitoring personnel will continue to evaluate groundwater TOC and TOX data to determine what course of corrective action to take on this issue.

Of the CY2013 split sample results, 19.9% met the evaluation criterion and 86.4% of those results met the precision criterion. This success rate for split sample results is in keeping with historical trends for split samples and indicates reasonable analytical agreement between laboratories. The metals analyses constituted most of the split failures and may have resulted from samples swapped either in the field or in the laboratory, heterogeneous distribution of metal-containing particulates between the split samples, and/or possible dilution errors at the time of analysis.

F.11.4 Laboratory Quality Control

Overall, the frequency at which laboratory QC samples were analyzed met the requirements of DOE/RL-91-50 and CHPRC-00189. About 98% of laboratory QC sample results met requirements. This indicates reasonable control of sample preparation and analytical methods at the laboratories with respect to cleanliness, precision, and accuracy. Section F.9 discusses the laboratory QC associated with groundwater monitoring samples in detail.

Of the laboratory MBs, 98.1% met the QC requirements. This indicates adequate cleanliness during laboratory sample preparation and analysis. Numerically, most of these failures were for the ICP metals with 275 of 6,353 blank results (4.3%) exceeding QC criteria. By percent, the general chemical parameters experienced the highest out-of-limit rate with 30 of 299 MBs (10.0%) exceeding QC criteria. Most of these MB failures were associated with alkalinity, total dissolved solids, and total organic carbon.

As a measure of analytical accuracy, 99.4% of the results for LCS, 97.8% of the MSs, and 98.8% of the surrogates met QC requirements. This indicates that the analytical methods are yielding adequate accuracy for the groundwater monitoring program.

With respect to analytical precision, 99.1% of the LCSDs and MSDs met QC precision requirements, while 97.9% of sample duplicates and 95.1% of surrogate duplicates met QC precision requirements. These precision results indicate that the analytical methods are producing groundwater monitoring data that meet groundwater monitoring precision requirements.

F.11.5 Laboratory Performance

The blind standards program and the performance evaluation studies provided an additional check on laboratory performance.

For the blind standards program, two laboratories, TARL and TASL, each had one quarter during CY2013 in which the laboratory did not meet the 80% success rate criterion defined in CHPRC-00189. Other issues observed as a result of the blind standards program are:

- *TOC*: TASL and WSCF both returned some high TOC recoveries during the reporting period, although TASL appears to have corrected their TOC issue.
- *Nitrite*: GEL, TASL, and WSCF under-reported the concentration of nitrite in a Hanford-Site groundwater matrix when the concentration of nitrite is near the laboratories' detection limits.
- *Boron*: TASL reported high boron results by ICP-MS; the laboratory plans to report future boron determinations by ICP-AES to overcome this issue.
- *Uranium*: With two exceptions, GEL, TARL, TASL, and WSCF reported blind-standard uranium results that trended high during the reporting period. A corrective action is in place to determine the source of these high uranium results.
- *Carbon-14*: During CY2013, TARL showed much improvement in its recoveries of carbon-14 in the blind standards; this was attributed to improved sample preparation equipment and procedures.
- Gross alpha: TARL and WSCF reported gross alpha results that trended low with 15 of 24 recoveries less than the lower recovery limit; GEL reported gross alpha recoveries well within the recovery limits. A corrective action is in place to determine the cause of the low recoveries for gross alpha at TARL and WSCF.
- *Iodine-129*: GEL and TARL reported iodine-129 results that trended high during the reporting period.

• *Plutonium-239*: During CY2013, GEL, TARL, and WSCF all reported plutonium-239 results that trended low; two precisions that exceeded the precision criterion were also noted.

These issues will continue to be monitored during and corrective actions sought as warranted.

The results of the performance evaluation studies indicate that the participating laboratories are, overall, providing analytical results within acceptable accuracy limits for analytes of interest to groundwater monitoring.

F.11.6 Conclusions

Based on this DQA, sample results appear to accurately represent target analyte concentrations in Hanford Site groundwater, and the analytical data are sufficient in quantity and quality to be usable for the groundwater monitoring program. The percent useable data for the CY2013 groundwater monitoring data set is 97.4%; this easily exceeds the DOE/RL 91-50 groundwater monitoring requirement of 85% data usability. Furthermore, 98.5% of the laboratory QC samples met QC requirements. This high rate of acceptable laboratory QC results indicates that laboratory accuracy, precision, and contamination control during sample preparation and analysis support the use of the data set for the groundwater monitoring program. Field QC samples were collected and laboratory QC samples were analyzed at the frequencies required in DOE/RL 91-50 and CHPRC-00189. Corrective actions have been initiated for systematic discrepancies displayed in the blind standards program for uranium and gross alpha.

F.12 References

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